APPLICATIONS OF RADIOISOTOPES TO PROBLEMS IN SOLID STATE PHYSICS

Thesis

Submitted by

Leslie W. Barr,
B.Sc.

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PREFACE

The research described in this thesis was carried out in the Department of Natural Philosophy under the direction of Dr. A.F. Brown and in the National Physical Laboratory under the supervision of Dr. M.C. Inman. A paper based on the results described in Chapters II and III is to be submitted to Physical Review. A note based on the technique developed for the evaporation of radioactive metal (Chapter V) has been accepted for publication by the Journal of Scientific Instruments. It is intended to publish a paper based on the results described in Chapter V.

CHAPTER I

INTRODUCTION AND HISTORICAL REVIEW

1.1. General

During recent years much interest has been shown in the field of diffusion in metals and in particular in the measurement of diffusion coefficients as a means of studying the defect structure of metals. In the following discussion the development of the subject is treated historically in order to show how this came about and to indicate the main advances in the subject.

1.2. The period till 1945.

The first treatment of diffusion was due to Fick[1] who put forward the relation (Fick's Law)

$$J = -D \frac{\partial c}{\partial x} \qquad (1)$$

where J is the flux of material per unit time through unit area perpendicular to the x axis, at a point where the concentration gradient is $\frac{\partial c}{\partial x}$. D is called the diffusion coefficient and is measured in $cm.^2$ $sec.^{-1}$. If the substance in which the diffusion is occurring is anisotropic three diffusion coefficients are required. The negative sign indicates that the diffusion flow takes place down the concentration gradient. Equation (1)

applies only to stationary flow, and a more general form may be derived by considering the rate of accumulation $\frac{\partial c}{\partial t}$, of the diffusing material in an element of volume, which gives the equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) \qquad (2)$$

If D is not a function of concentration, this gives

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (3)$$

Most diffusion measurements are carried out using boundary conditions for which equation (3) is fairly easily soluble.

The earlier measurements made of diffusion coefficients[2,3] had, of necessity, to be made by chemical techniques involving fairly large changes in chemical concentration. The measurements thus made, although of considerable technical interest, were not of sufficient accuracy to inspire any great theoretical interest in the mechanism of diffusion. This work revealed, however, one of the most striking features of diffusion coefficients, namely the nature of their temperature dependence. Diffusion coefficients all obey the Arrhenius form:

$$D = Do \exp^{\frac{-Q}{RT}} \qquad (4)$$

where D is the diffusion coefficient, D_o is called the frequency factor and Q the activation energy.

The assumptions involved in the derivation of equation (3)

(a) That the driving force for diffusion is the gradient of concentration,

(b) That the diffusion coefficient D is not dependent on the concentration,

are obviously satisfied by the self diffusion of pure metals. The possibility of such measurements had to wait for the introduction of radioisotopes. The earliest measurements made on self diffusion used naturally occurring radioactive elements as tracers. The experiments were performed on lead[4] and bismuth[5] using thorium B and thorium C as the diffusing substance. Such measurements of self-diffusion also avoided the difficulty inherent in chemical methods of the possible variation of the coefficients with chemical concentration. That such an effect occurred was shown by Matano in 1937[6]. Using the data of Grube and Jedele[7] on the copper-nickel system he demonstrated the tenfold variation of D with concentration. This kind of behavior was found in all the alloy systems investigated by the Matano analysis, thus revealing the difficulty inherent in chemical methods.

1.3 The period since 1945.

The comparatively ready availability of radioactive isotopes after 1945 resulted in a revival of interest in diffusion, principally self diffusion in pure metals,[8]

but also in alloys.[9] The improvements in experimental techniques due to the introduction of radio-isotopes and the use of increasingly pure and carefully prepared specimens roused interest in the atomic mechanism of the diffusion process in metals.[10]

The most important advance made, other than the introduction of radio-isotopes, was the discovery in 1947 of the Kirkendall effect by Smigelskas and Kirkendall.[11] The results of these authors showed that the rates of chemical diffusion of copper and zinc in brass are not equal. The method used was to place thin molybdenum wires on opposite faces of a rectangular bar of brass which was then electro-plated with copper. After heating to allow diffusion the bar was sectioned, and the distance between the opposite brass-copper interfaces, as indicated by the molybdenum wires, was measured. This distance was considerably less than the original distance before heating, by an amount greater than could be accounted for by diffusion controlled changes in density. This experiment has been repeated for copper-zinc and other binary alloys by da Silva and Mehl.[12] They found that the marker movement was independent of the material used for the markers, and was proportional to the square root of the time of anneal. This suggests that the marker movement is closely related to diffusion and the observed mass flow relative to the original interface of the diffusion couple can only be explained by assuming that the alloy components are

diffusing at different rates. If this is so the atoms cannot be diffusing by a direct interchange mechanism but must move either interstitially or by exchanging places with vacant lattice sites.

Additional light has been thrown on the mechanism of diffusion under the conditions obtaining in the Kirkendall type experiments, by work which is well illustrated by the experiments of Barnes[13] on copper-nickel couples. Barnes used specimens made from piles of alternate copper and nickel strips, welded together by hot pressing or rolling. After a diffusion anneal he observed an increase in the dimension parallel to the diffusion direction. A slight increase was also observed in the direction perpendicular to the diffusion direction. The dimensional changes were found to be proportional to the square root of the annealing time, thus indicating a connection with diffusion processes. The changes were much greater than could be accounted for by lattice parameter variations with chemical composition. Microscopic examination of sections made in a plane parallel to the diffusion axis, revealed small voids near the original interface on the side from which, on the hypothesis of a vacancy interchange mechanism, there is a net loss of atoms and a net gain of vacancies. The total volume of the voids was roughly of the value necessary to explain the macroscopic increase in size of the specimens. The voids were also found to lie on a plane perpendicular to the diffusion axis, and parallel to the original interface,

but about 40 microns from it.

It would appear that on the side of the original interface from which there is a nett loss of atoms, a sufficient supersaturation of vacancies may be attained so that voids can be formed either by nucleation on specks of impurity, or by direct condensation.

Similar results have been obtained by other workers.

1.4. Theoretical Development.

The results of these experiments allow the question of the actual atom transport mechanism to be discussed. The various models proposed from time to time for the basic process in pure metals and substitutional alloy diffusion:

(a) Direct interchange of nearest neighbours.
(b) Exchange with vacant lattice sites.
(c) Movement via interstitial sites.
(d) Ring rotation of atoms.

are shown diagrammatically in Figure 1 for the case of a two dimensional simple cubic lattice.

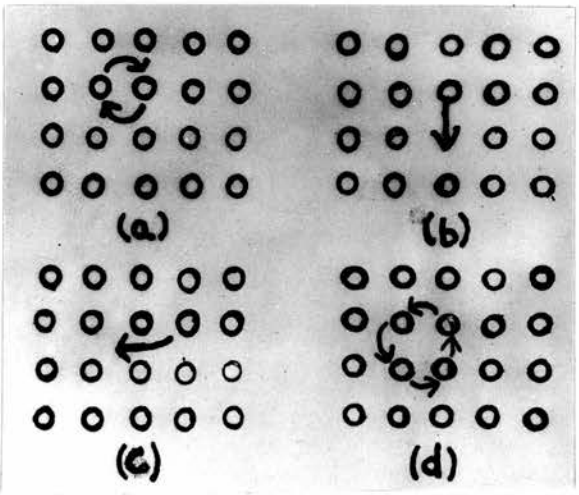

Figure 1.

Theoretical attempts have been made to estimate the activation energies associated with these models but the large approximations necessary have rendered difficult any detailed intercomparison of the theoretical with the experimental results. It has been possible, however, to eliminate some of the proposed mechanisms as being very unlikely in certain cases.

In the particular case of copper, calculations have been made by Huntington and Seitz,[14,15] on the basis of the quantum theory of solids. The energies for the vacancy, interstitial and direct exchange models have been calculated. The results are given in the adjoining table.

Theoretical Energies in K. Cal. mole.$^{-1}$

	Direct Interchange	Interstitial	Vacancy
Energy of ion-core repulsion	130	100	-10
Electrostatic energy	110	0	370
Energy to expand or contract electron gas	-	170	-170
Initial result	240	270	190
Result after redistribution of electron gas	-	210	30

The experimental value for the activation energy of self diffusion of copper is 47 k. cal. mole.$^{-1}$[16]

The results quoted above seem to rule out the mechanisms of direct interchange (the special case of

ring rotation) and interstitial diffusion, at least for the case of copper. Taken in conjunction with the Kirkendall effects results in face centred cubic metals, including the porosity occurrence, it seems likely that diffusion in the face centred cubic metal is a vacancy controlled phenomenon.

Using the model of vacancy diffusion, the diffusion coefficient at any temperature can be written:

$$D = \overline{\nu}\, a^2 = V \nu_D a^2 \exp - \frac{F_M}{RT} \qquad (5)$$

where $\overline{\nu}$ is the mean frequency with which an atom changes its position in the particular region of the lattice under consideration, and a is the distance which it moves. The factor $\overline{\nu}$ can be further broken down into the product of the atomic concentration of vacancies V, and the frequency with which it changes its position. The discussion by Le Claire[17] shows that it may be permissible to write the jump frequency of the vacancies as the product of a characteristic atomic frequency (ν_D the Debye frequency) and a reaction rate theory term $\exp - F_M/RT$, where F_M is the activation energy for the movement of a vacancy. In thermal equilibrium the density of vacancies is controlled by a Boltzmann factor $\exp - \frac{F_F}{RT}$, where F_F is the free energy of formation of a vacancy. Taking all these factors together the equation is

$$D = \nu_D a^2 \exp \frac{-(F_M + F_F)}{RT} \qquad (6)$$

In this equation both F_M and F_F are the temperature dependent free energies. It is suggested by a more detailed analysis that the internal energies E_M and E_F may be used if a factor 20 is introduced to account for the entropy term in the free energy, so that the equation is finally, after the substitution, $F = E - TS$:

$$D = 20 \nu_D a^2 \exp \frac{-(E_M + E_F)}{RT} \qquad (7)$$

Diffusion measurements can only give the value $-(E_M + E_F)$.

Most of the measurements of self diffusion coefficients have been made with the purpose of obtaining experimental values of the frequency factor D_0 and the activation energy Q, with a view to comparing them with the theoretically calculated values obtained by arguments similar to the one outlined above. The state of this branch of diffusion work can best be indicated by quoting from one of the most recent of these papers[18].

"Okkerse has gone to considerable trouble to compare recent self diffusion data on face-centred cubic metals with theoretical treatments of diffusion. Such treatments seek to prove the constancy of certain quantities involving D_0 and Q, by inserting them into the experimental values of D_0 and other physical properties. However, Okkerse found it impossible on these grounds to decide which theoretical approach gave the best description of the experimental results.

The authors have independently evaluated the same

'constants' using more recent and extensive data and have been forced to the same conclusions."

1.5. Short Circuiting Diffusion Paths.

The above theory will also apply to any regions in the metal where diffusion can occur at a rate different from that in the normal material. It has been shown experimentally[19,20] that such paths exist in the form of grain boundaries and dislocations. If satisfactory measurements are to be made the existence of such channels must be guarded against.

In general these short circuiting paths possess lower diffusion activation energies than those applicable to the normal lattice. Any interference from such channels would therefore show itself as anomalously high values of the diffusion coefficient at low temperatures.

1.6.1. Diffusion in Systems with Non-equilibrium Concentration of Vacancies.

While the detailed mechanism of diffusion is still in doubt it is possible to draw certain conclusions about vacancy concentrations from equation (7).

The equation can be written

$$D = D_0 \exp^{-\frac{E_M}{RT}} \exp^{-\frac{E_F}{RT}} \qquad (8)$$

and any alteration of the metal which has the effect of changing the vacancy concentration in the metal will have

a direct influence on the $\exp -\frac{E_F}{RT}$ term, the $\exp -\frac{E_M}{RT}$ term, the movement activation energy being unchanged. Thus the measurement of the diffusion coefficient under various conditions provides information about vacancy concentrations under these conditions. The exponential dependence of the activation energy makes variations in activation energies more easily detectable than variations in the D_o term, which is very difficult to evaluate accurately.

1.6.2. Methods of Introducing Excess Vacancies.

The behaviour of vacancies in metals has recently been reviewed[21]. The principle methods of introducing vacancies, other of course than those in thermal equilibrium, are:-

(1) Irradiation.

(2) Quenching from high temperatures.

(3) Plastic deformation.

A recent review of the effect of quenching and neutron irradiation on diffusion[22] suggests that the diffusion coefficient in copper would be altered very little by such treatment. Any change produced would appear only at low temperatures (about 400°C in the case of copper) where no swamping by "thermal" diffusion occurs. Even then the mean diffusion length is only about 1 μ. Such a small diffusion length necessitates special methods of measurement, a simple application of the

solutions of Fick's equation being unsuitable.

The case of plastic deformation appears to be much more amenable to experimental examination. Numerous phenomena have been observed in metals which can be attributed to enhanced diffusion under plastic deformation or to vacancy super-saturations. Among these phenomena may be listed the Portevin-Le Chatelier effect[23], intercrystalline cracking[24], strain-ageing[26] and enhanced rates of precipitation in alloys.[2(]

1.6.3. Generation of Point Defects by Plastic Deformation.

Experiments on the deformation of metals at low temperatures[27] and the observation of the subsequent behaviour on annealing by means of their electrical resistivity, have indicated that point defects (vacancies and interstitials) are generated by plastic deformation. The energy considerations mentioned earlier suggest that vacancies should be generated preferentially. This conclusion is supported by measurements of the activation energy and temperature of annealing of the defects which agrees with those estimated for vacancies by other methods.

Numerous theories have been put forward as to the mechanism of generation of the vacancies and various equations relating the concentration of vacancies to the plastic strain have been suggested. No definite

conclusion seems to have been reached, although all authors seem to favour a mechanism involving intersecting dislocations.(28)

At temperatures of about 400°C and higher the generation of vacancies by working may be large enough to effect the activation energy of other processes involving vacancies.

Such a process is the strain-ageing of metals, which has been explained theoretically as due to the diffusion of solute atoms to dislocations, thus locking them. Measurements of the activation energy of this process show it to be lower than the estimated diffusion activation energy in the alloys in question. This may be due to the generation of vacancies by the straining of the metal, the resulting supersaturation showing itself in the lowering of the activation energy of diffusion of the solute atoms.

Any supersaturation of vacancies in metals may also show itself by the appearance of voids in the metal formed by the condensation of the vacancies, as in the Kirkendall effect. Such a phenomena has been observed when various metals and alloys are slowly strained at high temperatures.(24) The voids so formed are found at grain boundaries, and are presumably formed by the condensation of excess vacancies on trapping sites at grain boundaries.

1.6.4. Direct Measurements of Enhanced Diffusion Rates.

Several experiments have been made on the diffusion of metals under deformation. The self diffusion coefficient of α – iron under compressive creep has been measured[29] but the results obtained have recently been withdrawn.[30] A study has also recently been made of the self diffusion of silver in both compressive creep and torsional experiments.[31] The results of this latter work indicates that the diffusion coefficient increases linearly with strain, the effect being more marked at lower temperatures.

Experiments of this type have the merit that they can in some cases differentiate between vacancy supersaturations and other defects, such as grain boundaries or dislocations, which have already been shown to influence diffusion by lowering the diffusion activation energy.

1.6.5. Outline of the Present Work.

The extension of measurements of the diffusion coefficient under plastic deformation to the case of copper seems useful, both on account of the large amount of information available about copper and because of its great practical importance.

The case of copper is also of interest as two of the effects mentioned above as being explicable on the vacancy generation theory have been observed in copper.

These are

(1) Intercrystalline cracking in copper and in α-Sb alloys[32].

(2) Strain-ageing in copper antimony alloys[25].

The system is also important because of the interest recently shown in the diffusion of traces of impurity in copper and silver and in the theories developed to account for the observed effects[33]. Experimental measurements of the diffusion of antimony in silver have been made and the extension of these to copper seemed desirable.

From the point of view of experiment the measurement of antimony diffusion is rendered comparatively simple because of the existence of the convenient isotope of antimony, Sb^{124}, which has a 60 day half-life and is readily available with high specific activities.

The first step in the measurement of any enhancement of the diffusion of antimony in copper is the determination of the value of D_o and Q for the case of static diffusion, that is diffusion through the action of thermally generated vacancies only. The determination of these quantities was carried out at the National Physical Laboratory and the experiments are described in Chapters II and III.

CHAPTER II

THE EXPERIMENTAL METHOD

2.1. Solution of the Diffusion Equation.

The most usual method of determining diffusion coefficients is to measure the concentration of the diffusing material as a function of its distance from some reference plane. The most convenient arrangement, both from the experimental point of view and for the ease of the subsequent calculations, is the diffusion into either an infinite or semi-infinite plane.

Crank[34] gives solutions of Fick's equations for these cases as

$$C = \frac{C_o}{\sqrt{4\pi Dt}} \exp \frac{-x^2}{4Dt} \qquad (9)$$

for the case of diffusion from a plane into an infinite solid and

$$C = \frac{C_o}{\sqrt{\pi Dt}} \exp \frac{-x^2}{4Dt} \qquad (10)$$

for the case of a semi-infinite substance. C is the concentration per unit volume of the diffusing substance at a distance x from the origin plane after a diffusion anneal of time t, C_o is the initial concentration per unit area of the diffusing material at the origin plane, D is the diffusion coefficient of the material.

In the case of self diffusion the above equations can be derived by considering the diffusion as occurring

by a random walk mechanism, for the atom jumps can be considered as being just as likely to occur in a positive as in a negative direction, the successive jumps not being correlated. In the case of random walk in one dimension of a given atomic species Chandrasakhar[35] has given the equation

$$p(x,t)dx = \frac{1}{\sqrt{2\pi n a^2 t}} \exp\frac{-x^2}{2a^2 n t} \cdot dx \qquad (11)$$

where p(x,t) is the probability that a given atom is in the interval between x and (x + dx), 'n' is the number of jumps the atom makes per unit time, a is the jump distance, and t is the time. The equation defining the diffusion coefficient of the atom species is

$$D_x = \frac{1}{2} n a^2 \qquad (12)$$

where the subscript x refers to the x direction. Equation (11) may then be written

$$p(x,t)dx = \frac{1}{\sqrt{4\pi D_x t}} \exp\frac{-x^2}{4D_x t} \cdot dx \qquad (13)$$

In the case of three dimensions, the probability (p.dv) that an atom is in the volume element dx.dy.dz = dv at (x,y,z) is given by the product of the three equations of the type of (13), one for each of the principle axes, giving

$$p.dv = \frac{1}{\sqrt{4\pi D_x t}} \cdot \frac{1}{\sqrt{4\pi D_y t}} \cdot \frac{1}{\sqrt{4\pi D_z t}} \exp -\left(\frac{x^2}{4D_x t} + \frac{y^2}{4D_y t} + \frac{z^2}{4D_z t}\right) \cdot dv \qquad (14)$$

It is sufficient to consider the diffusion occurring by motion along the three principle axes of the ellipse defined by D_x, D_y, D_z. The orientation of the ellipsoid is determined by the crystal symmetry. In the cubic lattice $D_x = D_y = D_z$ and $x^2 + y^2 + z^2 = r^2$, the ellipsoid becomes a sphere, and in this special case the diffusion is isotropic. Equation (14) can thus be simplified to

$$p.dv = \frac{1}{(\sqrt{4\pi Dt})^3} \exp\frac{-r^2}{4Dt} \cdot dv \qquad (15)$$

When the diffusion takes place in one dimension in an isotropic material and if there are C_o atoms per unit area at the origin, the number per unit volume at the plane x is given by the product of (p.dx) and C_o. Thus

$$C = \frac{C_o}{\sqrt{4\pi Dt}} \exp\frac{-x^2}{4Dt} \qquad (16)$$

or for diffusion in one direction

$$C = \frac{C_o}{\sqrt{\pi Dt}} \exp\frac{-x^2}{4Dt} \qquad (17)$$

This equation applies to the present work, where the diffusion is from a layer of the active material into a thick block.

It is convenient at this point to introduce the quantity $\sqrt{2Dt}$, the mean diffusion penetration when the diffusion coefficient has the value D and the time of anneal is t. This quantity corresponds to the standard deviation of the error curve which has the same

equation as (17). The value of introducing this variable is that it measures the order of magnitude of distance that an average atom wanders from its starting point by random migration, and hence enables estimates of the distance over which the concentration of the diffusing atoms can change during a diffusion anneal. For example, if the diffusion coefficient has a value of about 10^{-11} cm.^{2}/sec., then to give a penetration of about 10^{-2} cm., an annealing time of about two weeks is necessary. It is this small penetration and its square root dependance on the time of anneal, which makes the measurement of diffusion coefficients difficult, at any but high temperatures, where the value of the diffusion coefficient is comparatively large.

In the present work the concentration gradient of radioactive material is measured by means of a sectioning technique. If mechanical sectioning is used, as in Chapter II of the present work there is an upper limit of about 2.10^{-3} cm. on the thickness of the section that can conveniently be removed. If a lower limit to the number of sections is set at ten, then for an annealing time of two weeks there is a lower limit of 10^{-10} — 10^{-11} cm.^{2}/sec. to the diffusion coefficient which can conveniently be measured.

2.2. Experimental Technique.

The diffusion of antimony in copper is not, in the normal sense, self diffusion. If, however, advantage is

taken of the high specific activity with which antimony can be obtained, it is possible to use very low antimony concentrations. Thus, although the initial diffusion may involve concentration changes, for most of the diffusion time the antimony concentration is small and essentially the self diffusion of antimony in copper is being measured. A similar measurement has already been made of the self diffusion coefficient of antimony in silver. All the measurements were made with antimony contents well below the solubility limit.

2.2.1. Specimen preparation.

Cylindrical single crystals, grown by the Bridgman technique from 99.99% purity electrolytic copper, were used in order that the diffusion coefficient could be determined over as wide a range of temperature as possible without interference from grain boundary diffusion; this effect becomes increasingly important at low temperatures. The wide temperature range is necessary in order to enhance the accuracy of the measurement, especially the D_o value.

The single crystals, mounted in wax in square brass channeling, were sawn, in the grown condition, into sections about $\frac{3}{4}$ inch long and $\frac{3}{4}$ inch in diameter, using a jeweller's saw with fine oil as the lubricant. One face of each crystal was ground flat and smooth on a fine carborundum wheel using a plentiful supply of

water as coolant and lubricant. The grinding was done in such a way as to make the cylinder axis accurately perpendicular to the crystal face. The work-hardened layer formed during the lapping process was removed by electropolishing the crystal in an orthophosphoric acid solution (900 gm./litre) at a voltage of 1.5 volts. The polishing was continued for about seven hours at the end of which time about 0.005 inch thickness of copper had been removed. X-ray back reflection pictures were taken of the crystal surface to verify that the worked layer had been completely removed. The electropolishing had the effect of rounding the edges of the crystals but the central portion, which is used in the diffusion measurement, was left accurately flat. During the electropolishing the sides of the crystal were protected with a quick drying varnish (Cutex Nail Varnish). Before the next stage in the preparation of the specimens, the copper was cleaned by careful washing in A.R. benzene.

2.2.2. Antimony Evaporation.

Two single crystals were used to measure the diffusion coefficients at each temperature. The electropolished faces of each pair of crystals together with a thin glass slide, were simultaneously coated with spectroscopic purity radioactive antimony in a vacuum evaporation unit, the electrodes being placed symmetrically with respect to the evaporating electrodes.

This method of specimen preparation has recently been used in the measurement of the self diffusion of

gold[18] and the results obtained compared with these from specimens prepared by electroplating with the active material. No difference could be detected between the results obtained by the two methods. In the present case the vacuum evaporation method was selected because of its extreme flexibility in handling different metals without the requirement of different, sometimes difficult to handle, plating solutions. The vacuum evaporation of antimony is particularly simple in view of its low melting point (631°C) and its high vapour pressure (10 microns of mercury at 678°C).

Contamination of the vacuum apparatus was avoided by protecting the steel base plate and the electrodes with aluminium foil. The glass bell jar was readily cleaned with dilute acid. This method of active evaporation was used in the earlier experiments. An improved technique which avoided the long decontamination necessary with the above method was subsequently developed and will be described later.

The radioactive antimony deposited on the glass slide was used to estimate the initial concentration and thickness of the layer on the specimens. The radioantimony on the slide was dissolved in a mixture of equal parts of concentrated nitric and hydrochloric acid, the solution transferred to a precision glass weighing bottle and made up to a volume of 3 ml. The counting rate obtained from this solution was compared with that obtained from a solution made up by dissolving a known weight of radioactive antimony in concentrated

nitric hydrochloric acid. This result together with the known area of the slide and the density of the antimony, enables the thickness of the antimony layer to be calculated. This makes a very simple method for the measurement of the thickness of any vacuum evaporated film for which a convenient radio-isotope exists. The method is independent of the thickness of the deposited layer and is sensitive even in the range of thickness between 0 and 200 Å, the thickness used, where other methods are difficult to apply. The greatest uncertainty in the method is the value used for the density of the evaporated material, for this may be considerably different from that of the bulk substance. The results obtained from these measurements are given in Table 1. together with the thickness obtained by the use of the formula for evaporation from a point source.

$$T_P = \frac{m}{4\pi r^2 \rho} \cos\theta \qquad (18)$$

where

T_P is the film thickness at P.

m is the mass of the evaporated material.

ρ is the density of the evaporated material.

r is the distance from P to the evaporation electrode.

θ is the angle of inclination of the plane surface containing P to the molecular rays emitted by the source.

2.2.3. Diffusion Anneal.

Each pair of activated copper crystals was placed, active face to active face, in a copper cylinder of internal diameter ¾ inch and the ends of the cylinder closed with two tightly fitting plugs. The temperature of the specimens was measured with a thermocouple (Johnson Matthey platinum 13% platinum-rhodium) fitted into one of the copper plugs, as shown in Figure 2.

The assembly was then placed in a low temperature gradient furnace controlled by a platinum resistance thermometer to within ± 1°C. During the diffusion anneal the temperature of the diffusing couple was constant, as measured by the thermocouple and a precision potentiometer, to better than ± 1°C. Although the outer surface of the copper holder oxidised during the anneal, no trace of oxide was ever observed in the interior, when the active specimens were removed for sectioning. The diffusion anneal was terminated in each case by pushing the specimen holder out of the furnace into a bucket of water. In this way the necessity of a correction for the annealing time to allow for cooling was avoided.

2.2.4. Sectioning and Counting Technique.

After the diffusion anneal the specimens were sawn from the holders and each mounted in a lathe with its active face accurately perpendicular to the lathe axis.

Each crystal was first reduced in diameter to about 0.5 inch, to avoid surface effects. Sections of 0.002 inch were then taken and the metal turnings of each section collected in glass weighing bottles placed in turn under a funnelled hole at the bottom of a perspex collecting box (Figure 3), which enclosed the specimen and the cutting tool; a fine brush was used to sweep the turnings into the weighing bottles.

The thickness of the slices to be taken, except the first, was determined by advancing the lathe saddle by the required amount, this being measured on a dial gauge firmly attached to the lathe bed and with its probe touching the face of the saddle. The thickness of the first cut, which is important as it determines the origin from which all distances are measured, was found from the weight of the first section and the mean weights of the other sections each of which represented a known penetration into the specimen. This procedure was found to be necessary because attempts to determine the origin as the position at which the cutting tool appeared to make first contact with the crystal surface were not successful; the weight of the first cut, determined by advancing the lathe saddle a distance measured by the dial gauge, differed considerably from the weight of subsequent sections determined by the same procedure.

In the case of the three highest temperature anneals, those at 898°C, 955°C, 1002°C, this procedure was not

necessary as the specimens welded together, active face to active face. These specimens were mounted in the lathe and turned down to 0.5 inch and sectioned from one end. The centre of the activity - penetration curve was assumed to coincide with the original crystal faces and the diffusion coefficient estimated on this basis.

The contents of each weighing bottle was weighed and then dissolved in 3 ml. of a hydrochloric/nitric acid mixture delivered from a burette. This mixture was selected as being suitable for holding both copper and antimony in solution. The activity of each bottle was measured by counting the activity of the antimony in the bottle. This avoided any loss of activity due to the transfer of the solution from one container to another. Drop by drop delivery of the acid from the burette eliminated any loss of activity by spray during the dissolving of the metal turnings.

The actual counting was done by placing the weighing bottles in a brass holder, at the centre of a ring of six geiger counters in close packed formation. The counters were connected in parallel to a single scaling unit. The thickness of the brass holder was such that all the particles were stopped by the walls so that only the γ-rays and the annihilation radiation were detected. This arrangement has the additional advantage that the counting rate is proportional to the number of

geiger counters in operation, if these have matched characteristics. All the activities were measured to a statistical accuracy of ± 1% except at the tail of the penetration curve, where the weakness of the activity would have made such a determination very tedious.

A sodium iodide thallium activated crystal scintillation counter was used for five of the diffusion runs. The crystal was of the "well" type and the above procedure was followed in preparing the samples for counting. The higher counting rates obtained with the scintillation counter speeded up the counting operation and enabled deeper penetration curves to be taken.

Irradiation of antimony produces two radioactive isotopes

$$Sb^{121}(n,\gamma) \longrightarrow Sb^{122}$$

$$Sb^{123}(n,\gamma) \longrightarrow Sb^{124}$$

To simplify the counting technique, the 2.8 day antimony isotope was allowed to decay before any activity measurements were made.

Antimony, Sb^{124}, Decay Scheme.

Production Process. $Sb^{123}(n,\gamma)$ Sb^{24}. Half Life 60 days.

Thermal Neutron Absorption Cross Section (Natural) Element 5.5. barns.

Specific Activity (1 week at pile factor!) 1 mc/gm.

β-Activity		γ-Activity	
0.28 Mev	(12%)	0.60 Mev	(100%)
0.63 "	(56%)	0.99 "	(5.4%)
1.07 "	(4%)	1.38 "	(6.2%)
1.68 "	(6%)	1.71 "	(46%)
2.39 "	(22%)	2.11 "	(10%)

2.3. Surface Losses.

The analysis of preliminary diffusion runs indicated that some antimony evaporated from the specimen surfaces and was deposited on the internal surfaces of the copper containers. This loss of activity shows on the diffusion curves as an initial flat portion on the curve, as in Figure 11, or in some cases as an initial increase of activity with penetration (Figure 12). To prevent this antimony evaporation the later diffusion experiments were performed with a 100 Å layer of spectrographic quality copper evaporated on top of the antimony layer. The remainder of the experiment was then carried out as has been described. With this procedure the surface loss was much reduced. This technique also reduces the possibility of the blocking of the antimony at the surface by the formation of oxide layers.

CHAPTER III

Results & Conclusions

3.1. Results.

The measurements of the diffusion coefficients of antimony in copper were made at nine temperatures between 600°C and 1000°C.

Equation (17) was used to analyse the data. This equation is valid provided $h^2/12Dt \ll 1$, where h is the thickness of the evaporated active layer. This equation is satisfied in all the measurements described. For each anneal the logarithm of the specific activity, (counts $min.^{-1}$ $gm.^{-1}$), was plotted against the square of the penetration. The diffusion coefficient was derived from the slope of the resulting straight line.

Values of the activation energy Q and the frequency factor D_o were obtained by plotting the diffusion coefficient D at any temperature against the reciprocal of the absolute temperature.

3.2. Corrections.

3.2.1. Expansion.

The penetration distances used in the analysis of the experiments should be those at the diffusing temperature, whereas all the measurements were made at room temperatures. The use of room temperature distances

results in an error of about 4% at the highest temperature used and about 2% at the lowest. There appears to be no information available on the linear expansion coefficient of copper above 500°C so a considerable extrapolation is necessary. The experimental results of Nix and MacNair[36] were used to calculate the correction. The results are indicated in Table 1 and Figure 4 indicates the extrapolation made.

3.2.2. Time to Temperature Correction.

At higher temperatures and short annealing times, when the time for the specimens to reach temperature is appreciable compared with the annealing time, a correction must be applied to the time to give an effective annealing time t_e. Thus

$$\int_{t=0}^{t=t} D.dt = D_e t_e \qquad (19)$$

where D is a function of temperature given by $D = D_o \exp \frac{-Q}{RT}$

$t = t$ is the time when the specimen reaches the operating temperature T_e, D_e is the diffusion coefficient at that temperature. This gives

$$t_e = \frac{\int_0^t \exp \frac{-Q}{RT} dt}{\exp \frac{-Q}{RT_e}} \qquad (20)$$

t_e can be evaluated from this equation using an approximate value of Q. The integral is evaluated graphically

from the temperature measurements made during the heating up of the specimens.

A cooling correction is not necessary since the specimen is quenched from the annealing temperature in a few seconds. The method used in this graphical evaluation is illustrated in Figure 5 for the case of the highest temperature run, at 1002°C, using a value for Q of 40,000 cal. mol.$^{-1}$. The line AA' in the figure represents the new origin of time.

3.3. Tabulation of Results.

The results obtained from the experiments are summarised in the graphs in Figures 6 to 16. Details of two typical experiments are given in Tables 3 and 4, the plot of specific activity against penetration for the experiment at 898°C. being shown on Figure 13. In the case of the diffusion measurements at 653°C one of the crystals was sectioned taking a .001 inch cut and the other taking the normal .002 inch cut. The results of this diffusion measurement are shown in Figure 7 and Figure 8.

Table 5 and Figure 17 summarise the data from all the experiments and illustrate the temperature dependence. In all cases the method of least squares was used to calculate the results.

3.4. Discussion of Errors.

Sources of Error.

3.4.1. Curvature of the crystal face.

The error from this source is small because of the precautions taken in the preparation of the specimens.

3.4.2. Measurement of the diffusion anneal time.

The error in this becomes relatively more serious for the high temperature experiments, because of the shorter annealing times required for a given penetration. Corrections were applied in all cases for the time required for the couple to reach the diffusion temperature. If this correction is accurate to about 10%, then the total annealing time uncertainty would be about 0.25% for the case of the largest correction, which was about 2.5%, in the case of the run at 1002°C.

3.4.3. Measurement of the diffusion temperature.

In all the experiments the diffusion temperature was held constant to ± 1°C. The effect of temperature variations upon the diffusion coefficient is given by

$$\frac{dD}{D} = \frac{Q\,dT}{RT^2} \qquad (21)$$

In this case where Q is about 40,000 cal. mole.$^{-1}$, then at the lowest temperature used in this series of

experiments, 600°C., a variation of ± 1°C. leads to an error of 1.2% in D. The thermocouple used in the series of experiments was guaranteed to ± 1°C. This must be taken into account in the temperature uncertainty.

3.4.4. Alignment of the couple for sectioning.

The couple must be accurately set up in the lathe, so that the sections are accurately parallel to the original surface. Any misalignment causes an apparent increase in the penetration of the active material. It was found that it was fairly easy to line up the specimen with the surface perpendicular to the lathe axis. The possible error due to any misalignment of the specimen has been estimated by Shirn and Huntingdon.(37) In the present experiment the error from this source was thought to be small.

3.4.5. Determination of the section thickness.

The section thickness was determined by means of a dial gauge. It was estimated that the gauge measured accurately to about ± 2%.

The chief difficulty and source of uncertainty in the experiment lay in the nature of the metal used. Copper is a notoriously difficult metal to machine and well-annealed copper single crystals are even less convenient for the purpose of fine machining. The act of facing well-annealed copper single crystals of the type

used in the experiment produces a burr round the circumference of the crystal. This burr grows in size as successive facing cuts are made and at any time the burr is liable to contain material from previous sections smeared into it. Each cut made removes some of the metal from the burr with the result that activity measurements made on the turnings are not truly representative of the activity of the specimen at the position at which the cut is made. This would tend to give a slightly high value of the diffusion coefficient. LeClaire et al.[18] describe a technique, used in the measurement of the self diffusion of gold, for overcoming this defect in measurement of diffusion in very ductile metals. In this work the effect of burring was kept as small as possible by use of very sharp cutting tools of a suitable shape.

An examination of the weights of the sections, given in the tables of results, shows a scatter of about 5%, a scatter that is of a magnitude much greater than that possible from the dial gauge readings. This scatter is almost certainly due to the burring of the metal. The size of the error from this effect is difficult to estimate, but should not produce an effect of greater than about 4% in each diffusion coefficient.

3.4.6. Radioactivity measurements.

Errors in this may be due to the normal counting statistics or to the presence of interfering impurities

in the irradiated antimony. So far as the counting errors are concerned, the activity of each section was determined to ± 1% except at the tail of the penetration curves where the activity was falling to the normal background level. The number of sections available was generally sufficient to enable a reliable estimate of the diffusion coefficient to be made without taking into account the low activity sections at the tail of the penetration curve.

An examination of the impurities present in the spectrographic purity antimony indicates that no serious errors should be caused by the activity of impurities diffusing at a rate different to that of the antimony.

3.4.7. Errors due to other causes.

The outstanding remaining source of error is in the presence in the copper of short circuiting paths for diffusion. The use of single crystals eliminates, as has already been pointed out, the effect of grain boundary diffusion. There is still however the possibility of diffusion down dislocation pipes[38]. Any such effect should show itself as anomalously high D values at low temperatures[39]. No such behaviour was in fact observed.

Taking all these sources of error into consideration the expected error in the diffusion coefficient amounts to about 4-5%. This agrees well with the observed

scatter in the pairs of results taken at each temperature, with the exception of the results at 758°C and 806°C. In these two cases the large difference is believed to be due to the occurrence of unusually thick first sections.

3.5. Conclusions.

The rates of diffusion of a number of impurity elements in copper are summarised in Table 6.

For a copper solvent the theory of Lazarus[33] suggests that for a screening radius of 0.55 Å, the activation energy difference between impurity diffusion and the solvent self diffusion will be given by:

$$Q_{solvent} - Q_{impurity} = 3.36Z$$

where Z is the valence difference between impurity and solvent atoms. An improved version of Lazarus' treatment has been made by Alfred and March[40], using Z's based upon the Periodic Table valences of the impurity elements. It is clear from Table 6 that neither theory gives a satisfactory description of the results, although there is qualitative agreement between experiment and theory in that negative Z values lead to slower diffusion and positive Z values to faster diffusion than the solvent copper.

The suggestion of Mercer and Shuttleworth[41] that atomic size is the important factor is to a certain

extent substantiated in that the activation energy for diffusion decreases with increase of atomic diameter. The more rapid diffusion of the larger impurity atoms would appear to mean a lower vacancy formation or migration energy next to these atoms as a consequence of the relief of lattice strain near a large foreign atom.

CHAPTER 4.

Development of Polishing Technique
RESULTS AND CONCLUSIONS

4.1. It seemed desirable to continue the enquiry into the diffusion of antimony into copper and in particular to extend the research to the case of diffusion under plastic strain. Unfortunately information was lacking when the experiments were started as to the most suitable conditions for observing the effect, if indeed it existed. It was however possible to determine in a qualitative way the most suitable experimental arrangements by a consideration of the available diffusion and other data.

4.2. Specimen Preparation.

As has already been pointed out the diffusion coefficient is proportional to the vacancy concentration and to enhance the effect of any non-thermal equilibrium vacancies, it is desirable to keep the vacancy concentration as high as possible, for as long as possible. Trapping sites for vacancies must therefore be removed from the specimen, or at least kept in as low a concentration as possible.

Recent research indicates[42] that the main centres for the production of vacancies during annealing are grain boundaries. Similarly it is to be expected that grain boundaries will act as sinks for excess vacancies. The experiments, already mentioned, on the formation of

voids at grain boundaries on slow plastic deformation indicate that this effect does occur. Other evidence to substantiate this hypothesis lies in the observation [43] that vacancies, introduced into a metal by quenching, have shorter lifetimes in a metal which has been slightly deformed, that is having an increased dislocation density. It has been suggested that this is due to the action of dislocations as trapping sites for vacancies. Since grain boundaries can be regarded for many purposes as dislocation walls, the above experiments indicate that grain boundaries act as sinks for the annihilation of vacancies. For this reason single crystal specimens are the most suitable for observing any effect on the diffusion coefficient of vacancies formed by plastic deformation.

The use of single crystals for the experiments has the additional advantage that possible spurious diffusion down the grain boundaries is eliminated and that the deformation of single crystals has been extensively studied. This latter should make any results obtained more readily interpretable.

Since dislocations act as trapping sites for vacancies, it would be expected that careful handling, such as is necessary in the investigation of the easy glide region in the linear extension of single crystals, would be desirable. However, since the experiment involves the deformation of the crystals and the temperatures used are such that easy climb of any dislocations

will always occur, excessive care need not be taken in the handling of the crystals.

4.3. Experimental Conditions.

Diffusion measurements are essentially measuring the integrated results of a large number of atom movements and for any conventional measurement the conditions must be held constant over a long period; at least a day for most systems. Thus the conditions of plastic deformation must be held constant. This requires that the deformation be at an extremely low rate, if the specimen is not to be heavily deformed. If the boundary conditions indicated earlier are to be applicable, this must not occur. There is no record of any attempt to define a solution of the diffusion equation suitable for conditions of variable geometry.

Some numerical estimates can be made at this point. If a total deformation of about 10% is accepted as a convenient upper limit and a diffusion time of about one day is considered, then, for a specimen length of about 1 cm. the required rate of deformation is about 10^{-6} $sec.^{-1}$ It is of course convenient to have available a series of strain rates near this figure in order to study the influence of the rate of strain on the diffusion.

A theoretical study has recently been made of the effect on diffusion coefficients of irradiation-generated

vacancies[22]. While this is not of direct applicability to the present experiments the general nature of conditions established for the observation of any effect are of importance. The conditions required are that the temperature should be sufficiently high for the strain-deformation generated vacancies to be mobile, but not sufficiently high to lead to their swamping by thermal vacancies. The numerical estimates for copper lead to a value of about 400°C. for this optimum temperature. A similar argument[44] based on the results of for diffusion of iron under compressive creep, leads to the same temperature. Too much weight must not be placed on the latter argument since the results on which the estimate was based have since been withdrawn. It does seem likely however that a low temperature would be best.

The proposed mechanisms for the generation of vacancies by plastic deformation are obscure[28] but such theories as there are all involve intersecting dislocations. The available estimates[45] are applicable only at low temperatures and indicate that the number generated should only produce a very small diffusion effect, but the situation may be somewhat different at high temperatures, where the slip mechanism may be different and dislocations can climb freely, emitting vacancies.[46] If the optimum condition, for vacancies to be generated, is intersection of dislocations, then the best form of deformation is one involving intersecting

slip and specimens oriented for slip on more than one system would be best.

To summarise, the best conditions for the observation of any enhanced diffusion during plastic deformation are:

(1) Use of single crystals deformed in slow constant strain.

(2) Times of deformation of about one day.

(3) Use of low temperatures.

(4) Slip on intersecting systems.

The measurement of diffusion coefficients at low temperatures presents difficulties which are apparent from the work already described. In particular, if times of about one day and temperatures of about 600°C are used, the formula for the mean penetration gives a distance of penetration of about 10 microns. This small penetration necessitated the development of techniques other than mechanical sectioning.

4.4. Development of Technique.

The most reliable techniques, developed for the measurement of diffusion coefficients, have all been based on sectioning methods. For this reason it seemed that a method based on a refined sectioning technique would be best. Several experimenters have used, or suggested, methods of determining impurity concentrations,

based on sectioning using chemical attack. The self diffusion of gold has been measured[47] by means of a technique based on dissolving layers of gold from a foil made of an activated film of gold plated with inactive gold. No details of the solvent used in this experiment are given in the paper, although the success of the technique is dependent on the evenness with which the solvent attacks the surface. A similar technique has been used for the measurement of zinc concentrations in the surface layer of copper single crystals, which were then used to determine the effect of such zinc concentrations on the mechanical properties of copper.[48] In this case the zinc concentration was measured using a polarographic method. Again no details are given of the etchant used. Another method based on X-ray analysis of exposed surfaces has been proposed; in this case the suggested method of attack was electropolishing.[49] Recently an etching technique has been used[50] to examine the segregation of phosphorous at the grain boundaries of ~~the~~ iron. The phosphorous concentration was measured by counting the β radiation from the active phosphorous. The iron concentration was determined by a colorimetric method. In all these cases the thickness of the layers was determined by chemical analysis of the solutions obtained after the chemical attack in order to obtain the total quantity of material removed from the surface, the thickness then being calculated from the known surface areas and densities.

The points requiring consideration in order to use chemical attack to measure diffusion coefficients are:

(1) A method for dissolving thin layers from copper without pitting and uneven attack.

(2) A method of estimating the amount of material removed from the surface.

The use of electrolytic chemical polishing for the removal of thin (1 micron) layers in the present experiment was considered but general handling difficulties ruled this out. A purely chemical polish has been proposed for use with copper[51] and a test of this showed that it produced a very smooth mirror finish to the copper surface. The convenience of such a polish was such that it was used throughout the experiments to be described, for the preparation of smooth surfaces on copper. The composition of the polish is given in the adjoining table.

Chemical Polish

1 part concentrated Analar nitric acid.
1 part concentrated Analar phosphoric acid.
1 part concentrated Analar acetic acid.

The method of use is to immerse the copper to be polished, in the solution, which is kept at a temperature of between 60 and 70°C, for about ten seconds. It was found in practice that the use of the polish in the concentration given above resulted in the removal of layers of about 20 to 30 microns thick. For this reason

the above solution was diluted, in the proportion of one part of solution to one part of water, for the removal of the thin layers in the determination of the diffusion coefficients. Once the amount of copper removed from the surface is known the thickness of the layer can be calculated from the known density of vacuum cast copper (8,90 gms./cc.) and the surface area of the specimen. For the specimens used in the present experiments, rectangular blocks, the surface area can be measured fairly accurately using microscopic methods. The chief difficulty is in the measurement of the amount of copper removed from the surface, for, if the surface area of the speciman is about 2 $cm.^2$ and the layer removed is to be about 1 micron, then the weight of copper is about 2 mgm. The technique developed for this determination is described in the next section.

4.5. Copper Determinations.

4.5.1. General Experimental Technique.

(1) The distilled water used was distilled in a commercial "Manesty" still.

(2) All the glassware used in the experiments was cleaned in the following way. The glassware was allowed to stand overnight, in chromic oxide-sulphuric acid cleaning mixture, rinsed thoroughly with distilled water at least three times, and then dried in a laboratory oven at about $70^{\circ}C$.

(3) All the volumetric apparatus used was calibrated by weighing with distilled water. In all cases this was done until a reproducible technique was developed.

(4) Analar grade reagents were used throughout.

(5) All transfers of solutions except where specifically mentioned were carried out using 1 cm. diameter glass tube drawn out to a fine (~ ½ mm.) capillary and fitted on the 1 cm. end with a rubber eyedropper.

(6) To reduce experimental errors the same cells, volumetric flasks, pipettes and stock solutions were used throughout.

4.5.2. Analytical Method.

Among the various methods available for the estimation of milligram quantities of copper in solution may be mentioned microvolumetric and gravimetric analysis, absorptiometric and polarographic techniques.[52] The polarographic method has the disadvantage, in application to radioactive solutions, that contamination of the electrode system can occur.

The simplest method would appear to be the absorptiometric method, which offers the advantages of ease of calibration, the minimum of handling and high accuracy. The standard absorptiometric techniques for the determination of copper are not suitable for the present work as they all involve considerable preliminary chemical extraction.[52] There is, however,

available for copper the readily formed complex cupammonium ion with its strong blue colour. The preliminary work was done using this complex and a Unicam G.P. 300 colorimeter.

4.5.3. Work Using the G.P. 300 Colorimeter.

The basis of all absorptiometric techniques is the comparison of the absorption of the unknown solution, prepared by standardised methods, with the absorption of known standard solutions. The comparison is made by setting the instrument for complete absorption, that is no light reaching the detector, and complete transmission, with light reaching the detector through the solvent used in the particular case under consideration. The scale is then calibrated in percentage transmission, or in units of optical density D, given by

$$D = \log_{10} \frac{I_0}{I} \qquad (22)$$

where I_0 is the incident light intensity and I the light intensity transmitted by the copper containing solution under consideration.

The optical absorption coefficient, ϵ , is defined by the equation

$$\log_{10} \frac{I_0}{I} = D = \epsilon c l \qquad (23)$$

where c is the concentration of the absorbing substance in solution, and l the length of the absorption cell. In the present work the cell length was 1 cm. For substances obeying Beer's law ϵ is a constant independent of concentration. This is, of course, the most convenient case from the practical point of view as the concentration of the material in solution can readily be determined from equation (23) once the absorption coefficient is known, without any necessity for graphical procedures.

The detector used in the measurements with the G.P. 300 was a photocell, the light being selected by means of a filter. This meant that the absorption coefficient was not that for a single wavelength but for a broad band of wavelengths.

4.5.4. Preparation of Standards.

The standards were prepared by dissolving small quantities (~150 mgm.) of copper, cut from the stock used to prepare the specimens, in 100 ml. of the polishing solution. Small volumes of the resulting solution, in 0.5 ml. steps from 0.5 ml. to 5 ml., were taken from this stock solution and pipetted into standard weighing bottles, 3 cm. diameter, 6 cm. tall, the solutions being made up in each case to 5 ml., using copper free polishing solution. The series of solutions so obtained were then evaporated, using an infra-red lamp, till only phosphoric acid was left. This was

done in order to reduce the volume of the solutions and to remove as much acid as possible from the mixture, which had of course to be made alkaline at a later stage in the process. No great care was necessary in the evaporation since phosphoric acid is not evaporated by an infra-red lamp. It was however convenient to keep a check of the evaporation to save time. This was done by gently blowing ammonia fumes over the solutions. If there was still nitric or acetic acid evaporating from the solutions a white cloud of ammonium nitrate or ammonium acetate appeared above the bottles. Time was saved during this stage of the preparation by drying the solutions in batches of twelve, one of which was a blank solution containing no copper.

The solutions, prepared as described, were then neutralised using concentrated ammonia; the liquid being added very gently to the solution using glass droppers. This stage in the process had to be performed with great care in order to prevent overheating and splashing of the solution. The addition of the ammonia was also critical for the pH of the solution had to be adjusted to give the required ammonium complex, which could be recognised by its characteristic colour, without precipitating ammonium phosphate.from solution. It was found extremely difficult to do this and it was frequently necessary to warm the solutions in order to drive off the surplus ammonia. The solutions were

transferred from the weighing bottles to 10 ml. volumetric flasks and made up to 10 ml.

The absorption of the standard solutions was measured using glass cells and a red filter. The curve obtained is shown in Figure 19. It is seen that Beer's law is obeyed over the whole range of concentration. From this curve the copper concentration of any solution, prepared by a similar method, can be determined. The accuracy of this method, using the G.P. 300, is about ± 2%.

The difficulty which lead to the abandonment of this method of analysis was that mentioned above, of obtaining the required ammonium complex without precipitating ammonium phosphate. It was found that not only did this precipitate interfere with the colorimetric determination by absorbing and scattering the incident light, but some copper was lost from solution by co-precipitation.

An attempt was made to eliminate the interfering phosphoric acid by the following procedure. After the solutions were concentrated by evaporation, concentrated potassium iodide was added to precipitate the copper. This fine precipitate was centrifuged down and the supernatant phosphoric acid drawn off by glass dropper. The precipitated copper was then redissolved in nitric acid, again evaporated down to a small volume and treated with ammonia. It was not necessary to remove the phosphoric acid completely, but only to reduce its

concentration below the level at which it would cause precipitation in the alkaline solution.

This attempt failed because it was found that some of the copper was not precipitated by the potassium iodide and was removed with the phosphoric acid. This complicated procedure would also have been ruled out on account of the amount of handling necessary for each sample.

These experiments indicated that a technique which did not require the phosphoric acid solution to be made alkaline would be useful. The literature(53) suggested that a sensitive colouring agent for copper was hydrobromic acid. This was tried but it was found that, except at ice temperatures, free bromine was liberated from solution and made colorimetric measurements impossible. Strong hydrochloric acid has also been suggested as a suitable colouring agent for copper and trial of this showed it to be suitable, provided care was taken to remove all traces of nitric acid from solution to prevent the formation of the coloured nitrosyl chloride.

Investigation of standards, prepared as above, but with hydrochloric acid instead of ammonia, yielded the curve shown in Figure 19. The non-linear nature of this indicated that, except at extremely low concentrations, Beer's law did not apply. This made accurate measurements on hydrochloric acid solutions impossible. In view of this it was decided to abandon the use of the

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G.P. 300 and investigate the solutions with a Unicam S.P. 600 spectrophotometer, which has the advantage that the absorption coefficient is measured using a band width of about ± 3 mμ instead of the ± 100 mμ of a filter absorptiometer.

4.5.5. Work using the Unicam S.P. 600 Spectrophotometer.

The use of the S.P. 600 for high accuracy measurements has recently been reviewed by Davies and Prue.(54) They suggest that the principle sources of error in the use of this instrument are:

(1) spectral impurity of the light from the monochromater;

(2) multiple reflections of light from the absorption cell faces, causing light to pass several times through the cell;

(3) non-parallelism of the light used, causing errors in the effective length of the cell and a failure of some of the multiply reflected light to fall on the photocell of the spectrophotometer.

The authors suggest techniques for overcoming these sources of error. Their recommended procedure involves leaving the absorption cells permanently in position, in order to eliminate the error due to the cells being at different angles to the incident light. If this is done the chief remaining source of error lies in the multiple reflections from the absorption cells and the non-monochromatic nature of the light. These errors will occur not only in the unknown sample but also in the

standardising measurements and the comparison will be accurate provided the same experimental conditions are obtaining throughout. The authors suggest that this condition can be satisfied if the cells are modified so that they can be emptied and filled without removal from the cell holder. This prevented also the contamination of the solutions by dust, or the cell faces by grease or solution overflow.

The comparatively small quantities of solution available in the present work and the complicated handling necessary, ruled out their technique in this case. A modification of their method was however used. The cells were removed from the cell holder for filling and emptying but this was done entirely by the use of glass droppers. This, together with the precaution of keeping the bottles stoppered except when the dropper was being used to extract the solution, reduced the contamination errors. The absorption cells were also kept closed with glass caps, except when the solutions were being changed. The cells were washed out twice with each new solution when the solutions were changed, a clean dropper being used in each case. It was found by experiment, that the chief source of error in the present work was due to the contamination of the cell faces by solution overflow, hydrochloric-phosphoric acid solution being particularly greasy and difficult to remove by wiping the cell faces with lens tissue.

This source of error is removed by the above procedure.

The glass caps were also necessary in this experiment to prevent water vapour condensing into the strongly acidic solutions and the acid fumes damaging the cell compartment of the spectrophotometer.

The measurements were made using matched quartz cells, of 1 cm. optical length. The cells were compared with one another using blank solutions and the largest variation detected was about 0.2%. This was a variation at 100% transmission and can be regarded as negligible. A similar result was obtained by comparing the transmissions of blanks prepared during different "runs".

Experiment also showed that the results obtained were more consistent at a constant temperature. Since the behaviour of a highly ionised solution, of the type used in these experiments, is unlikely to be affected by temperature fluctuations of about 5°C. the causes of the variations are almost certainly instrumental. The possibility of such variations was ruled out by performing all the measurements with water from a thermostatic bath, circulating through the cell holder at 25 ± 0.2°C.

4.5.6. Calibration using the S.P. 600.

Standard solutions were prepared, as has already been described, with concentrated hydrochloric acid as the colouring agent. The absorption spectrum obtained

from one of the standards, using a non-copper containing solution taken through the same process as a reagent blank, is shown in Figure 20. It can be seen from this graph that a broad absorption peak exists from about 900 mμ to 1000 mμ , which is the wavelength limit of the S.P. 600. This absorption peak appears to be almost flat topped but a slight maximum was found at 920 mμ. This wavelength was therefore selected as being suitable for copper determinations.

The absorption spectrum of an ammoniacal solution of copper in phosphoric acid was also determined and is shown in Figure 18. A comparison of the spectra of copper in the hydrochloric acid and in the ammoniacal solutions, shows why the G.P. 300 proved unsuitable for the examination of the acid solution when it was so successful in the case of the alkaline solutions. The absorption band of copper in the ammoniacal solution is in the centre of the transmitted light for the red filter. (transmits from 600 to 800 mμ). In the case of the measurement of the transmission of the acid solution using the G.P. 300, the variation being detected was the movement of the base of the absorption bands as the concentration was altered, most of the transmitted light from the filter being of a wavelength for which the copper has zero absorption. Such measurements could hardly be expected to obey Beer's law. No filter was available having an absorption only in the region of 900 mμ.

The result of the measurements of the optical densities of a series of solutions, of differing copper concentrations, is given in Figure 21. Beer's law is clearly obeyed and use of equation (23) gives a value of 108.6 for the molar absorption coefficient. A more convenient way of stating the result was to use the equation

$$D = 0.171\,x \tag{24}$$

where x is the weight of copper in milligrams in a standard 10 ml. volumetric flask. The use of this equation was possible since the calibration of the flasks revealed that they contained the same volume to within 1 part in 300. This equation, which is accurate to $\pm$ ½%, was used to calculate the weights of copper in each solution.

Since the amount of copper removed in the polishing solution is not accurately controllable, occasionally a larger amount of copper is removed than can be measured accurately by the direct application of equation (23). In such cases the absorption of the unknown sample was measured relative to a previously determined standard instead of the usual blank. If the subscripts 1 and 2 refer to the known standard and the unknown sample respectively, then

$$\log_{10}\frac{I_0}{I_1} = \epsilon c_1 \ell$$

$$\log_{10}\frac{I_1}{I_2} = \epsilon c_2 \ell \tag{25}$$

$$\therefore \quad \log_{10}\frac{I_0}{I_2} = \epsilon(c_1 + c_2)\ell$$

and the quantities c_1 and c_2 can be measured in a region in which the spectrophotometer is at its most sensitive.

4.6. Diffusion Measurement Procedure.

The experimental technique employed was to pipette 10 ml. of the polishing solution into the precision weighing bottles mentioned earlier, warming the solution to about 60°C. on a hot plate then dipping the copper specimen to be analysed into the solution. It was found by trial that dips of about 6, 12 and 20 seconds removed roughly 1, 3 and 6 micron layers from the copper surface. The specimens were removed from the solution using stainless steel tweezers, which were not affected by the solution, and the specimens and the tips of the tweezers washed with a stream of distilled water; the washing water being allowed to run into the appropriate weighing bottle. The solution was then evaporated down as has been described, made up into 10 ml. flasks and the copper content measured using the spectrophotometer.

The antimony content was determined by measuring the activity of 5 ml. samples taken from the flasks and made up to 10 ml. with distilled water. The activity of the resulting solution was measured using a liquid counter (20th Century Electronics, Type M.6.) This procedure was adopted because of the high efficiency of this type of counter for the radiation from Sb^{124}.

Between each count of the active solutions the liquid counter was washed out several times with a strong solution of hydrochloric acid, followed by distilled water, then rinsed with alcohol and acetone. The counter was then allowed to dry before a background count was taken to check that all the active material had been removed.

4.7. Experimental Checks.

It was found during test runs with radioactive copper and antimony that there was no loss of material during any part of the procedure. In particular during the transfer of the solution from the weighing bottles to the volumetric flasks, the loss was less than one part in five thousand of the copper and antimony content. This loss was very much less than other errors occurring in the measurements.

An examination, using the spectrophotometer, of copper solutions containing traces of antimony showed that small quantities of antimony did not interfere with the copper determination.

CHAPTER V

APPLICATIONS OF THE TECHNIQUE

5.1.

The technique described in Chapter IV was tested by determining the diffusion coefficient of antimony in copper at three different temperatures between 640°C. and 540°C. This range was chosen to overlap the range of temperatures at which the diffusion coefficient had been measured using the proven method of mechanical sectioning, in order to provide a comparison.

5.1.2. Specimen Preparation.

The specimens used were copper single crystals grown using Bridgman's method from high purity copper sheet. (Appendix II). The crystals were grown in the vacuum (10^{-4} mm. Hg.) furnace shown in Figure 22 and Plate 1, by dropping graphite crucibles containing the copper at a slow rate (10 cms./hour) through a temperature gradient with a maximum temperature of approximately 1200°C. The crystals grown by this method were 8 cm. by 0.9 cm. by 0.3 cm. Specimens 1 cm. long were cut from these crystals using the cutter shown in Plate 2, the crystals being mounted for this operation in brass tubing with paraffin wax. The sectioning machine uses a high speed water cooled carborundum slitting wheel of 4 inch diameter and 0.015 inch thickness. This method of cutting single crystals was found

to be very satisfactory, the sectioned surface being smooth and not deformed by the cutting process. Since active crystals were also cut with this machine the water was prevented from spraying by enclosing the instrument in a perspex box and the waste water was filtered to trap any active particles.

After the crystals had been removed from the brass tubing by melting the paraffin wax they were cleaned in benzene and polished in the chemical polishing solution. Their surface areas were determined by measurements made with a travelling microscope.

For the purpose of evaporating thin layers of active antimony the crystals were gently clamped between two pieces of thin brass shim held in slight tension by means of brass nuts and screws. This was done to provide a convenient holder for the crystals during the evaporation. The evaporation itself was performed in the device shown in Figure 23(55), a general view of the evaporator is shown in Plate 3. An open ended glass tube of 5 cm. diameter contains a 2.5 cm. high, 1.5 cm. alumina crucible (Morgan Crucible Co. XN5), which is heated by the radiation from an 0.5 mm. diameter tungsten wire, passing through small holes blown in the sides of the glass tube. The active antimony is simply dropped into the crucible. The crystals to be activated are placed on a stand above the crucible; escape of antimony during the evaporation being prevented by closing the gap above the crystals by glass slides. This system has the

advantage over the method used earlier that decontamination of the vacuum system is unnecessary, the tube, glass slides and crucible being scrapable after each evaporation. This system was used to deposit~80 Å of antimony on four faces of the crystals, this being the number which could be covered without demounting the crystals from the holder.

After the antimony evaporation the crystals were coated with copper, by vacuum evaporation, to prevent antimony loss from the crystals during the anneal.

5.1.3. Diffusion Anneal.

Diffusion anneals were performed in an atmosphere of oxygen-free nitrogen (Appendix III), the crystals being contained in a graphite crucible in close contact with a platinum 13% rhodium-platinum thermocouple. The graphite crucible was contained in a silica tube which was closed with a steel top vacuum sealed to the silica with an O-ring and containing O-ring sealed openings for the thermocouple and the nitrogen supply system (Figure 24). When the crucible was placed in the tube and the seals made, the system was evacuated by a rotary oil pump and flushed several times with nitrogen, the last charge being allowed to remain in the tube under a slight (1 cm. of mercury) positive pressure. During the period of the anneal nitrogen, under this pressure, was allowed to bubble through the tube at a rate of about 5 ml./min.,

the flow rate being measured on the bubble flow meter and regulated by the valve system shown in the diagram.

The anneal was performed by sliding the silica tube into a low temperature gradient furnace, kept at a constant temperature by an Ether-Wheelco Capacitrol thermocouple operated controller, the Chromel-Alumel thermocouple being placed on the furnace windings. This system has the merit that although the controller only operated on a temperature variation of $\pm$ 5°C., this fluctuation was damped out at the specimen. The temperature was measured continuously during the heating up period and at regular intervals during the anneal.

The anneal was terminated by withdrawing the silica tube from the furnace. The specimen was cooled by playing the cold blast from a hair drier on to the tube. The low thermal inertia of silica enabled the specimen to be cooled to a temperature where the diffusion was negligible, in less than 5 minutes.

5.1.4. Analysis.

The diffusion specimens so obtained were analysed by dipping into chemical polish, as has already been described. Because of the labour involved in handling each sample the diffusion distance was always arranged to be approximately 15 microns. In this way there was appreciable variation in the activity of the samples, even when only ten layers were removed from the surface.

The time of dip was 8 to 12 seconds, as experience showed that this time resulted in the removal of approximately 3 microns layers from the surface.

5.2. Diffusion under Plastic Deformation.

5.2.1. Specimen Preparation.

The single crystals used in this part of the work were grown from the same copper sheet as was used in the static diffusion. The single crystals were also grown in graphite crucibles in the vacuum furnace described earlier. The specimens differed in that they were grown with a definite orientation and were grown in the shape of standard flat tensile specimens, the sizes being 10 cm. long by 1.6 cm. broad and 0.17 cm. thick. The crystals contained a thin centre section 2 cm. long and 0.65 cm. broad. This gauge length was connected to the ends of the crystal by smoothly curved shoulders. The purpose of this shape of specimen was to confine the plastic deformation to the gauge length, the thicker ends being intended to provide a large area for the gripping of the specimens in the constant strain rate apparatus. A clear idea of the specimen shape can be obtained from Plate 4.

The orientation was selected to satisfy the condition of slip on two systems mentioned earlier. Since this criterion does not define a unique orientation of the crystal with respect to the tension axis, the additional condition was imposed that the direction of slip should be contained in the plane parallel to the

tension axis of the crystal and perpendicular to the flat surface of the specimens. This was done to make the slip steps prominent on the crystal surface for microscopic examination and to restrict the deformation to two directions, i.e. along the tension axis and the diffusion direction. Measurements on the deformed specimens indicated that this condition was satisfied in the two specimens deformed at the lower strain rates but only partially in the case of the specimen deformed at 2.10^{-5} sec^{-1}.

All the crystals were grown from the same seed crystal in the crucible shown, with a crystal in position, in Figure 4. The method adopted to grow the crystal was to determine in a dummy run the boundaries of the zone in the furnace, run at a fixed power input, which was capable of melting copper. The crystal crucible was then placed in the furnace with the seed crystal intersected by the lower boundary and the remainder of the crucible closely packed with carefully cleaned copper sheet. The furnace was then brought up to temperature and the crucible dropped through the high temperature zone. When the crystal was removed from the crucible it was etched with a mixture of 1 to 1 nitric acid-distilled water. If the copper had not formed a single crystal the different grains showed up under the action of this etch by virtue of the different reflecting powers of the faces with different orientations. Crystals of the dimensions used in these experiments

were found to be very prone to growing in the form of bicrystals , with the grain boundary parallel to the extension axis of the crystal and a very small ($\sim 1^{o}$) orientation difference between the grains. Sometimes one of the grains was lost at the gauge length contraction of the specimen; when this happened the crystal was considered as suitable for use, otherwise it was passed through the furnace until it grew as a single crystal. It was found that specimens grown in this way had, if the surfaces of the graphite crucible were carefully polished with a soft cloth, a very smooth flat surface, ideally suited for microscopic observation with only a very short polish in the chemical polishing solution.

Holes were cut in the crystals at each end to hold the bolts used to secure the crystal in the straining machine. To prevent distortion of the crystals this was done by coating them with paraffin wax in which circular gaps were scraped at the required places. Each crystal with its wax protective coat was then immersed in strong (2 parts acid to one of water) nitric acid. This solution dissolved the required holes in ten minutes. The holes so obtained were only roughly circular but were satisfactory in practice. In some cases the crystal ends required trimming; this was done in the same way by cutting the wax away from the crystal surface along the line where the specimen was to be divided.

The single crystals were polished for a few seconds in the chemical polish and lines scribed on the surface at each end of the gauge length by pressing a razor blade on to the surface at right angles to the extension axis of the specimen. The line so obtained is clearly visible on the photograph in Plate 8. This photograph was taken after the specimen had been extended 28% in 8 hours at 598°C. The lengths between the fiducial marks was measured with a travelling microscope by setting the crosswires of the microscope on the intersection of the line with one of the edges of the crystal and traversing the microscope, so that the crosswires were always on this edge, until the intersection of the other line and the crystal edge came on to the crosswires. This technique ensured that the same length of crystal was measured each time. The particular crystal edge and crystal were identified by scribing a number on one of the ends.

The radioactive coating was applied to the flat top and bottom surfaces of the crystals in the unit described earlier; the crystals being supported in this case on microscope slides placed across the edges of the glass tube. These cover glasses served to screen the ends of the crystals from the evaporating antimony so that it was only deposited on the gauge length, leaving the ends of the crystal free for handling purposes.

5.2.2. Constant Strain-Rate Apparatus.

The constant strain-rate machine used in the strain anneals is shown in Figure 28 and in Plate 7. The arrangement of a horizontal straining machine and travelling furnace was adopted to enable the furnace to be brought up to temperature before being run over the evacuated steel tube containing the specimen. This procedure reduced the time taken for the system to come to a uniform temperature, an important point when anneals of only 8 hours are used. The constant strain rate was applied to the extension rod by means of a gear wheel on a screwed rod pressing via a ballrace, on to the steel plate of the apparatus. The gear wheel was turned by a worm from a reducing gear box, the variable speeds being obtained by controlling the input speed of the gear box by a pulley and belt system.

The low gradient furnace used was made from a silica tube wound with nichrome resistance wire and controlled by a platinum resistance element mounted near the furnace windings and operating a Sunvic R.T.2. Controller. This arrangement enabled the temperature of the specimen to be kept constant to $\pm$ 2°C.

The method of gripping the crystals for mounting in the straining machine is seen in Plate 5. The grips were made of heat resistant steel and the upper parts (the lower in the photograph), contained grooves machined in them to slide on the steel rods ~~in the steel rods~~ in

the straining machine; the method of securing them to the machine being to slip steel pins through holes drilled in the flats at the ends of the grips. These flats corresponded to flats on the central rods in the machine. The specimens were clamped between these grips and the upper blocks (in the photograph) by means of a stainless steel bolt passed through the two parts of the grip and the specimen. Good friction between the grips and the crystal was ensured by covering the inner faces of grips with saw cuts. Each part of the grips contained two stainless steel threaded rods screwed into it. The following procedure was devised in mounting the crystals in the grips to minimise the distortion. The grooved blocks were clamped, using the threaded rods, to a brass plate containing slots machined in it to allow the distance between grips to be adjusted according to the position of the holes in the crystals. The brass plate also contained a central slot running several inches into the plate from each end to accomodate the head of the crystal securing bolt. The crystal was carefully laid on and adjusted until the holes in the crystal and grips coincided. The remaining blocks were then placed on top and the securing bolts slipped into position and tightened. To do this it was found best to screw the bolts to thumb tightness, then clamp the assembly in a vice by the non-grooved blocks. This rendered the whole assembly immovable

and the bolts could be tightened up to full tension without distorting the crystal. The actual mounting in the straining machine was performed by laying the grip system complete with brass plate on to the rails of the straining machine, slipping the securing pins through the holes in the grips and straining machine extension rods and then removing the brass plate. The completed arrangement is shown in Plate 6. The thermocouples, used to measure the temperature of the specimens during the strain-anneal, can also be seen in this photograph. During the anneal the thermocouples were tied to the surface of the crystal, one at each end, by means of loops of thin tungsten wire.

5.2.3. Strain Anneal.

Because of friction and slackness in the machine a rather complicated procedure had to be followed when commencing the strain anneal. Once the crystal was in position in the machine the slackness was taken up by a hand operated wheel running on the threaded rod. The gear wheel was then set against the bearing face of the steel base plate and the worm engaged on to the gear teeth. The driving motor was then run at its highest speed until the dial gauge showed a change of reading. Since the dial gauge could be read to the nearest 0.01 cm., only negligible deformation was introduced into the specimen by allowing the motor to be run a little

beyond this position in an attempt to ensure that all the machine slack was taken up. The thermocouples were then tied into position on the crystal and the outer steel tube slipped over the specimen. Once this was evacuated the apparatus was ready to be raised to the annealing temperature.

The temperature of the specimen was recorded as it rose to the annealing temperature and the straining motor started when the temperature reached what experience showed was the corrected zero time for the diffusion anneal, the correction being obtained from preliminary experiment by the method previously described. The corrected origin of the diffusion anneal was calculated from the data obtained during the heating up period and was found to differ from the estimated zero time by never more than 3 minutes, a time which can be neglected in 500 minutes, which was the average total length of anneal. This method of judging the time to begin the straining of the specimen is valid, provided the mechanism of deformation did not change during the 20°C. between the temperature at which the motor was switched on and the final annealing temperature. The deformation and thermal diffusions were thus occurring over the same time. The ratio of the diffusion coefficients obtained from the measurements and the appropriate thermal diffusion coefficient will then have a precise meaning.

The diffusion anneal was terminated by sliding the

furnace from the steel tube and spraying the tube with large quantities of water. This quenching procedure cooled the crystal to temperatures where diffusion was negligible in less than 3 minutes.

The specimen was removed from the machine by re-clamping the grip system to the brass plate, the variable distance slots were useful at this stage, and removing the securing pins. The final dimensions of the crystal were measured before the crystal was removed from the grips for sectioning. The sectioning was performed on the machine previously described, the crystal being mounted during the operation between two flat plates of perspex held together with screws. The crystal was clamped between the plates with one of the end pieces protruding. The arrangement was then gripped in the vice of the cutter and the crystal end cut off, care being taken to keep the cut at right angles to the tension axis of the crystal. The system was then turned and the other end of the crystal removed. The gauge length of the specimen was then ready for chemical sectioning to determine the diffusion coefficient.

5.3.1. Results. Static Diffusion.

The results of three diffusion anneals at temperatures of 633, 567 and 540°C. are shown in Figures 25, 26 and 27; the numerical data is summarised in Table 1, and the temperature dependence is illustrated in Figure 32, together with the results obtained from three strain diffusion measurements. The line in this figure is the best straight line obtained from the earlier work. The results were calculated in the same way as the mechanical sectioning results with the exception that the section thicknesses and the specific activities were both calculated from the weight of the copper removed from the specimen. The method of calculating the best value of the diffusion coefficient from the data also differed, in that the best value of the coefficient was obtained by the centre of gravity method[56], instead of the least squares method. This method was adopted as being less time consuming than the least squares method and yielding the same result to within the limits of the experiments; as checks, using both methods on the same data, showed. The error quoted in each case corresponds to the 95% reliability limits.

5.3.21 Results. Strain Diffusion.

The results of three strain diffusion anneals are shown graphically in Figures 29, 30 and 31. All the above remarks apply to these results also.

5.3.22. Correction to Strain Diffusion Results.

As has been pointed out, the application of the normal method of calculating diffusion coefficients in the static case is not strictly valid when the diffusion specimen is subject to plastic deformation. However a correction to the value of the diffusion coefficient, obtained by the normal methods, can be calculated for the case of the type of deformation applied in the present experiments. If a rectangular co-ordinate system is set up with the z axis parallel to the tension axis of the specimen; the x axis perpendicular to the surface of the crystal (parallel to the diffusion direction); and the y axis parallel to the flat surface; then, if the strain in the specimen, defined as $\frac{dL}{L}$, is denoted by e and the strain rate $\dot{e}$ ($\frac{1}{L}\frac{dL}{dt}$); we have, because of the conservation of volume:

$$e_x + e_y + e_z = 0 \qquad (26)$$

and since in this case $e_y = 0$,

$$e_x = -e_z \qquad (27)$$

Two extreme possibilities can now be considered. Firstly if the specimen were to be extended and then the diffusion allowed to procede normally the correction is obviously zero. Secondly if the specimen were diffused then extended, all the x values would be diminished by a scale factor of $(1-e_x)$ or in this case by $(1-e_z)$. Since the diffusion coefficient is proportional to the square of the penetration, this means that in this case

the experimentally determined diffusion coefficient must be divided by $(1-e_x)^2$, to give the correct value of the diffusion coefficient. The case of constant strain must lie between these two extreme cases, the exact value depending on the type of averaging which a more detailed analysis would give. If we use the simplest averaging method the correction factor becomes $(1-\frac{e_x}{2})^2$ or to a first approximation $(1-e_x)$. The result of applying this correction factor is shown in Table 7. The condition that $e_y = 0$ was checked by measurement and was found to hold in the cases of the slower deformation rates. In the case of the deformation at $e = 2.10^{-5}$ sec^{-1}., the correction factor was modified by the appropriate amount to allow for the contraction of the specimen in the y direction.

5.4. Discussion of Errors.

5.4.1. Static Diffusion.

The sources of errors are substantially the same as those discussed in Chapter III, in so far as the errors due to the measurement of diffusion time and temperature, specific activity and diffusion short circuiting paths are concerned. The chief additional source of error in the present experiments lies in the sectioning technique and the method of its measurement.

5.4.12. Copper Concentration.

It was found possible to measure the copper concentration using the spectrophotometer to an accuracy of slightly better than ± 1%. The chief additional source of error is then the density of the copper: the value used in the calculations was that given in the table for high purity vacuum cast copper. This value was 8.90 gm./cm^3. It seems unlikely that this value would be incorrect to more than 1%. This means that the sources of error in the present technique are not more than those present in the mechanical sectioning work.

5.4.13. Surface Area.

Because of the squared dependence of the diffusion coefficient on the penetration distance any measurement

connected with the estimation of the penetration is of double importance. In this case the measurement subject to the greatest uncertainty is the surface area used in the penetration calculation. From repeated measurements made on the crystal, before and after polishing, the error in the surface area was estimated as ± 3%; this estimate could be subject to a systematic error because of surface roughness but information is lacking on the magnitude of this and on the influence such roughness might have on the chemical attack.

5.4.14. Edge Effects.

Sectioning using chemical sectioning has the defect that the sectioning is not confined to a flat surface where the diffusion is normal to the surface. In the specimens used the concentration at the edges of the specimens increased because of diffusion into the edge volume occurring from two directions. The magnitude of the error due to this effect can be estimated roughly as follows. The total length of edge in the specimens used was approximately 6 cm. If the region of overlap is taken as about 10 microns on each side of the edge, then the area influenced by the effect is 10^{-2} cm.^{2} Since the area of the specimen was normally 2 cm.^{2} the uncertainty introduced by this error is not more than 1%.

5.4.15 Antimony Concentration.

Because of the smallness of the penetration used in the chemical sectioning care had to be taken that the antimony concentration did not exceed a permissible level. As information regarding the variation of the diffusion of antimony in copper-antimony alloys was lacking this limit on the antimony concentration was arbitrarily set at 0.1 atomic per cent in the first section (the one with the highest antimony concentration.) A study of the variation of diffusion coefficients with composition in alloys in which this variation had been examined[6], showed that this estimate was not unreasonable. An estimate of the antimony concentration was made by weighing a very small piece of radioactive antimony and preparing standard solutions, as has already been explained. This showed that the maximum value of the antimony concentration was normally slightly less than 0.1 atomic per cent, except in the case of the strain anneal at a strain rate of 2.10^{-5} sec.$^{-1}$. In this experiment more than the normal amount of antimony was evaporated on to the specimen in order to allow activity measurements to be made deeper into metal than was normally the case, without increasing the counting time. In the case of this specimen the antimony concentration was 1 atomic per cent, at the surface. It is likely that the high value of the diffusion coefficient in this case may be due in part to this excessive antimony concentration, since, in view of the low melting point of antimony (630°C.), the value of the

diffusion coefficient would be expected to rise with increasing antimony concentration.

5.4.2. Strain Diffusion.

The sources of error special to this part of the work are involved with the strain anneals. The chief defect of the constant strain rate apparatus was that the exact time when the specimen began to deform was not accurately known. The procedure outlined in the experimental details was adopted in an attempt to overcome this uncertainty but a radical modification to the machine would be necessary to remove the defect completely. The strain rates used in the experiments are however unlikely to be in error by more than 20%.

The temperature measurement technique was considered to be accurate to $\pm 3^{\circ}C.$, this being the largest difference observed to exist between the temperatures measured by the different thermocouples.

5.4.3. Conclusion of Error Discussion.

A consideration of all these sources of error, in the case of both static and strain diffusion, leads to the conclusion that the uncertainty in the experimental results is approximately $\pm$ 10% or less than the uncertainty due to the uneven sectioning.

5.5. Discussion. Static Diffusion.

The graphs of the logarithm of the specific activity (counts $min.^{-1}$ $mgm.^{-1}$), shown in Figures 25, 26 and 27, for the case of static diffusion reveals a considerable scatter indicating that the method of attack by chemical polishing is uneven. The excellent agreement of the diffusion coefficient at 633°C., obtained by the method of chemical sectioning, with the results obtained by mechanical sectioning indicates that the chief danger of chemical methods of sectioning, namely of preferential attack, either on crystallographic faces of the crystal or at the edges of the specimen, is not occurring. The results at the lower temperatures give a much poorer agreement with the extrapolated high temperature results. The difference between the experimental results and the high temperature values is moreover too great to be explained by the scatter in the experimental data. The explanation must be sought in an undetected systematic error or the deviation must be considered to be real. In this connection an examination of the ln.D versus 1/T graph shows that the deviation of the low temperatures results from the high temperature extrapolation appears to be fairly uniform; the mechanical sectioned measurement at 600°C. the strain annealed measurements at 598°C. and the static diffusion results at 567 and 540°C. all appear to lie on a straight line suggesting that a process involving a higher activation energy

becomes predominant at low temperatures. While it is most unwise to draw conclusions from linearity in a logarithmic plot, it is possible that an effect may occur since any trend due to the action of dislocation pipes would be expected to enhance the diffusion coefficient and, as has already been pointed out, error due to systematically uneven sectioning would be expected to have the same result.

There is available a possible explanation of the reduced diffusion coefficient observed in the chemical sectioning as compared with the mechanical sectioning results. The diffusion in the chemically sectioned specimens is observed over a penetration distance of approximately 15 microns as against penetrations of 200 microns in the mechanical sectioning technique. Now experimental results on the annealing out of vacancies in quenched metals enables an estimate to be made of the mean number of jumps made by a vacancy before annihilation. The results so obtained all lead to the conclusion that in copper a vacancy makes 10^8 to 10^{10} jumps in its lifetime[21]. Thus in copper the mean free path of a vacancy, which is given approximately by the formula,

$$L = a\sqrt{n} \qquad (28)$$

where a is the lattice spacing and n is the mean number of jumps made during a vacancy lifetime, is between 10

and 20 microns. Since the surface of a crystal is an infinite sink of vacancies this means that the 20 micron layer at the surface of a metal would be expected to have a somewhat lower than normal equilibrium vacancy concentration and hence diffusion coefficient. It is however difficult to see why this reduced diffusion coefficient should appear only at low temperatures. This is obviously a field which needs more experimental study.

The conclusion to be drawn from the results of the static diffusion measurements is that whatever the behaviour of the diffusion coefficients at low temperatures, at temperatures near 600°C. the chemical polish allows of reasonably accurate measurements of diffusion coefficients to be made using penetration distances of only 15 microns. No other technique appears to offer this possibility.

5.6. Discussion. Strain Diffusion.

5.6.1. Surface Condition.

The most striking feature in the plots of logarithm of specific activity against the square of the penetration distance in the case of the experiments under strain, is the much better linearity of the experimental points. Since the only systematic difference in treatment was the performing of the strain anneals in a vacuum of 2.10^{-5} cm. of mercury, instead of in the oxygen-free

nitrogen used in the static diffusion measurements, the only conclusion to be drawn is that the vacuum annealed surfaces possess a structure which lends itself to very uniform attack by the chemical polish. This is not a surprising conclusion in view of the work on the thermal etching of metals in vacuum annealing[57].

5.6.2. Slip Behaviour.

Microscopic examination of the surface of the specimen before sectioning revealed that none of the specimens suffered from recrystalization and even in the case of the specimen extended 30% there was little sign of necking or of non-homogeneous deformation.

The slip line structure observed on the surface of the crystals seemed to vary in a random way despite the fact that the specimens had the same initial orientation to within 2 degrees. Typical examples of the slip patterns obtained are shown in Plates 9, 10 and 11. Figure 9 shows the slip band pattern obtained on a specimen deformed at 10^{-6} sec.$^{-1}$ at 700°C. The slip lines are very intense and spaced about 100 microns apart. This is typical of the patterns obtained on copper deformed in creep at these temperatures. The type of slip shown in Plate 10 was obtained on a specimen deformed at 3.10^{-6}sec.$^{-1}$ at 598°C. Traces of slip on two systems can be seen but one system is much more intense than the other. Figure 11 on the other hand

(strain rate 3.10^{-6}sec.$^{-1}$ temperature 594°C.), shows a fully developed system of intersecting slip bands. The reasons for the difference between the patterns is not clear but a possible explanation may be in slight orientation differences between the crystals. It is possible, however, that the explanation may lie in the fact that at the temperatures used in the experiments there will be little hardening on a given set of active slip planes. Thus once a system has begun to slip it will continue to do so indefinitely. If this is the case the slip band behaviour may be determined by chance to a considerable extent. In view of the small amount of work carried out on very low strain rates no definite conclusion can be reached on this point but more experiments on this type of deformation are certainly required.

One feature of the deformation which was unexpected was that the deformation was uniform over the whole of the specimen, despite the reduced cross-section at the gauge length. This made it impossible to work at very high strain rates as the gear system was designed to provide strain rates on a 2 cm. length, not on the approximately 7 cm. length between the grips. Future experiments could conveniently be made on short uniform strips of copper cut from one long strip of single crystal. This would also ensure exact duplication of orientation.

5.6.3. Effect on Diffusion of Plastic Deformation.

The results of the measurement of the enhancement of the diffusion coefficient are of great interest. The results of the present work suggest that there is little or no such enhancement. The measurements made at strain rates of 3 and 4×10^{-6} sec.$^{-1}$ certainly show no evidence of enhanced diffusion and the anneal at a strain rate of 2.10^{-5} sec.$^{-1}$ shows an enhancement of 2.5, where the results of Lee and Maddin[31] suggest that at such a strain rate and temperature an enhancement of at least 15 would occur. As has already been pointed out this measurement could be high because of the relatively large antimony concentration in the diffusion zone.

This negative result is in good agreement with recent measurements made on the diffusion of antimony in copper under creep conditions, using strain rates of 10^{-6} to 10^{-5} sec.$^{-1}$ [58], mechanical sectioning, and temperatures of 700 to 800°C. A similar result has been obtained in the case of silver. The self diffusion of silver in plastic deformation at strain rates of 1 to 25.10^{-5} sec.$^{-1}$ in both tension and compression has recently been measured, at 800 and 900°C.[59]. In this case also no enhancement of the diffusion coefficient was observed. These results obtained at a high temperature, taken together with the results quoted here for low temperatures, suggest that no enhancement of the

diffusion coefficient takes place except possibly at low temperatures and high strain rates and even in this case the effect is fairly small. The results obtained by Lee and Maddin are difficult to understand in the light of the experimental results quoted. It can only be assumed that the type of deformation used in their experiments (torsional strain) results in some effect which is not present in the linear extension experiments. It would be very useful if the chemical sectioning technique described here could be applied to torsion experiments.

5.7. Suggestions for Future Work.

5.7.1. Improvements in Technique.

The most useful improvement which could be made on the technique developed in this work would be directed towards reducing the amount of labour involved in making the measurements. It would reduce the handling labour if weighing bottles calibrated to hold 10 ml. were used. This would remove the necessity of transferring the solution from the weighing bottles, in which the chemical sectioning is performed, to the volumetric flasks. If this modification was combined with substituting a well-type scintillation counter, capable of holding the weighing bottles, for the liquid counter the efficiency of the counting process would be much increased and all the handling of the solutions, except that necessary for the spectrophotometric measurements, would be eliminated, with corresponding increases in speed and accuracy. If the labour could be reduced in this way it should be possible to handle much larger numbers of thinner sections with the attendant increase in accuracy, even if the experimental scatter could not be eliminated.

The observation made in the course of the work, that the vacuum annealed specimens showed much more even attack than those annealed in a controlled atmosphere, suggests that it would be desirable in future to perform all the anneals in vacuum. This might with

advantage be combined with a short vacuum anneal before the specimens were coated with the radioactive layer.

5.7.2. Future Work.

The most obvious experiment to attempt is to extend the measurements of the antimony diffusion to low temperatures to check whether the decrease in the diffusion coefficient is a real effect or whether some source of systematic error exists in the experimental technique at the lower temperatures. With the increased speed of measurement resulting from the suggested experimental improvements, it might be possible to combine measurements on the antimony diffusion with measurements of the self diffusion of copper, (half-life 10 hours) using the technique developed[9] for the simultaneous determination of the diffusion coefficients of metals with different half lives. This work could profitably be extended to the diffusion of iron and cobalt into copper as anomalous values in the diffusion coefficients have been detected for these systems.[39] It has been suggested that this may be due to dislocation diffusion.

APPENDIX I

Antimony Grain. Laboratory Report No. 10716.

	Estimated Quantities Present. (Parts per million.)
Iron	5
Copper	3
Calcium, Magnesium, Silicon, Silver, Sodium	each element less than 1

Elements sought for and not detected:

Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Hg, In, Ir, K, Li, Mn, Mo, Nb, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

APPENDIX II.

Copper Sheet: Laboratory Report No. 8110x.

		Estimate of Quantity Present. (parts per million.)
Iron		2
Silver		2
Lead		1
Nickel		1
Silicon		1
Sodium		1
Calcium, Magnesium	each element less than	1
Selenium, Tellurium	each element less than	0.0002%

APPENDIX III

Oxygen-free nitrogen

O_2 less than	1	(parts per million)
H_2 less than	420	(usually nil)
Ne less than	500	
He less than	1600	
A less than	60	
CO_2 about	20	
CO	nil	
H_2O about	0.01	gm./m^3.
Other gases	5	
N_2	the remainder.	

APPENDIX IV.

Since the correction factor for the evaluation of the diffusion under strain, mentioned in 5.3.22, was derived a fuller treatment has been published[63]. The equation derived in this work is, in the notation previously used:

$$\frac{c}{c_o} = \left\{\frac{2\dot{e}_x}{\pi D[1-\exp(-2\dot{e}_x t)]}\right\}^{\frac{1}{2}} \exp\left\{\frac{-\dot{e}_x x^2}{2D[\exp(2\dot{e}_x t)-1]}\right\} \quad (A.1)$$

For small strains and considering the experimental accuracy the exponential can be expanded as a power series in e_x, thus

$$\exp(2\dot{e}_x t) = 1 + 2\dot{e}_x t + 2\dot{e}_x^2 t^2$$

and

$$\exp(-2\dot{e}_x t) = 1 - 2\dot{e}_x t + 2\dot{e}_x^2 t^2 \quad (A.2)$$

If this substitution is made in equation A.1. and $\dot{e}_x t$ is put equal to e_x, then

$$\frac{c}{c_o} = \sqrt{\frac{1}{\pi D t(1-e_x)}} \exp\frac{-x^2}{4Dt(1+e_x)} \quad (A.3)$$

This reduces to the equation used in the normal analysis when $e_x = 0$. If natural logarithms of equation A.3 is taken we have:

$$\ln\frac{c}{c_o} = \text{constant} - \frac{x^2}{4Dt(1+e_x)} \quad (A.4)$$

and the gradient of the straight line obtained by plotting $\ln \frac{C}{C_o}$ against x^2 is, when it is remembered that in this case e_x is negative,

$$m = \frac{-1}{4Dt(1-e_x)} \qquad (A.5)$$

or

$$D = \frac{D'}{(1-e_x)} \qquad (A.6)$$

where D' is the diffusion coefficient obtained from the measured gradient. This is the same as the correction factor derived earlier and used in the evaluation of the results in Chapter V.

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TABLE 1

Weight of antimony in standard 1	29.94×10^{-6} gms.
Do. Do. Do. 2	132.04×10^{-6} gms.
Activity of standard 1	1574 ± 16 counts/min.
Do. Do. 2	7094 ± 71 counts/min.
Do. unknown	2823 ± 23 counts/min.
Weight of unknown sample, using 1.	$52.5 \pm 1.0.10^{-6}$ gms.
Do. Do. Do. 2	$53.7 \pm 1.0.10^{-6}$ gms.
Mean Weight of unknown	$53.1 \pm 1.0.10^{-6}$ gms.
Mean Area of slide	3.57 cm.^{2}
Assumed density of antimony (vacuum distilled)	6.62 gms. cm.$^{-3}$
Thickness of antimony film	224 ± 22 Å.
Thickness from formula	200 ± 35 Å.

TABLE 2.

Expansion Correction

Temperature °C	Estimated Coefficient of expansion $\times 10^5$ $^\circ C^{-1}$	Correction %
600	1.87	2.2
653	1.89	2.5
706	1.91	2.7
758	1.93	2.9
806	1.95	3.1
859	1.97	3.4
898	1.98	3.6
955	2.0	3.8
1002	2.02	4.0

758°C

TABLE 3

Crystal Section No.	Wt. of Metal gms.	Geiger Counter Background = 22 ± 0.5 c.p.m. Time from zero	count/min.	Count/min/gm. (Corrected for background & decay)	Section Thickness 0.002 inch Corrected penetration cm.	Corrected penetration cm^2 10^5	ϵn c.p.m/gm.
1.	0.1312	0	1583	12005	0.00427	1.82	9.393
2.	0.0694	20 min.	755	10562	0.01108	12.28	9.265
3.	0.0778	45 min.	730	9100	0.01616	26.12	9.116
4.	0.0624	33 h.20 min.	479	7372	0.02124	45.11	8.905
5.	0.1000	33 h.50 min.	555	5360	0.02632	69.27	8.587
6.	0.0664	35 h.	266	3705	0.03140	98.60	8.217
7.	0.0832	37 h.30 min.	226	2476	0.03648	133.08	7.814
8.	0.0765	38 h.15 min.	136	1503	0.04156	172.72	7.315
9.	0.0826	39 h.40 min.	92	860	0.04664	217.53	6.757
10.	0.0846	57 h.15 min.	65	520	0.05172	267.50	6.254

TABLE 4

Section No.	Wt. of Copper gm.	Scintillation Counter Background = 334 c.p.m. Time from zero	Count/min/gm. corrected	ℓn.c.p.m./gm/5	Section Thickness 0.002 inch Penetration from centre	Penetration $cm.^2.10^5$
1.	0.0578	0	66817	9.500	0.0441	194
2.	0.0456	5 min.	83772	9.726	0.0391	153
3.	0.0514	10 min.	103268	9.936	0.0340	116
4.	0.0518	15 min.	122471	10.106	0.0289	83.5
5.	0.0494	20 min.	144028	10.268	0.0238	56.6
6.	0.0586	25 min.	164352	10.400	0.0187	35.0
7.	0.0573	30 min.	183665	10.511	0.0137	18.8
8.	0.0550	35 min.	196909	10.581	0.0086	7.4
9.	0.0573	40 min.	203665	10.615	0.0035	1.22
10.	0.0405	45 min.	206494	10.628	0.0016	2.56
11.	0.0579	50 min.	206563	10.629	0.0067	4.5
12.	0.0538	55 min.	192751	10.560	0.0117	13.7
13.	0.0580	60 min.	180397	10.493	0.0168	28.2
14.	0.0541	65 min.	163549	10.395	0.0219	48.0
15.	0.0586	66 min.	141809	10.253	0.0270	72.9
16.	0.0550	70 min.	108964	9.989	0.0321	103.0
17.	0.0611	75 min.	92455	9.825	0.0371	138.0
18.	0.0547	80 min.	72084	9.576	0.0422	178.0

TABLE 5.

DIFFUSION OF ANTIMONY IN COPPER

Temperature °C.	Annealing Time sec.	Diffusion Coefficient $cm.^2\ sec.^{-1}$	Diffusion Coefficient Corrected for Expansion $cm.^2\ sec.^{-1}$
600	$3.63.10^6$	$0.975.10^{-11}$	$0.997.10^{-11}$
		$0.929.10^{-11}$	$0.949.10^{-11}$
653	$2.74.10^6$	$4.45.10^{-11}$	$4.56.10^{-11}$
		$4.39.10^{-11}$	$4.50.10^{-11}$
706	$8.58.10^5$	$1.43.10^{-10}$	$1.46.10^{-10}$
		$1.35.10^{-10}$	$1.39.10^{-10}$
758	$4.08.10^5$	$5.10.10^{-10}$*	$5.25.10^{-10}$*
		$4.33.10^{-10}$	$4.46.10^{-10}$
806	$2.59.10^5$	$0.944.10^{-9}$	$0.973.10^{-9}$
		$1.19.10^{-9}$*	$1.23.10^{-9}$*
859	$1.90.10^5$	$2.58.10^{-9}$	$2.67.10^{-9}$
		$2.63.10^{-9}$	$2.72.10^{-9}$
898	$9.34.10^4$	$4.63.10^{-9}$	$4.80.10^{-9}$
		$4.66.10^{-9}$	$4.83.10^{-9}$
955	$5.41.10^4$	$1.12.10^{-8}$	$1.16.10^{-8}$
		$1.08.10^{-8}$	$1.12.10^{-8}$
1002	$3.65.10^4$	$2.12.10^{-8}$	$2.21.10^{-8}$
		$2.24.10^{-8}$	$2.33.10^{-8}$

From these results $D_o = 0.34 \pm 0.12\ cm.^2\ sec.^{-1}$, $Q = 42.0 \pm 0.7$ k. cal. $mole.^{-1}$, for the measurements without the expansion correction. With the expansion correction the result is $D_o = 0.38 \pm 0.12\ cm^2\ sec.^{-1}$, $Q = 42.2 \pm 0.7$ k. cal. $mole.^{-1}$. The quoted errors refer to the 95 reliability limit.

* These results are believed to be in error because of excessively thick first sections.

TABLE 6.

Impurity Element	Reference	D_o cm^2 sec^{-1}	K cal.mole^{-1}	Assigned Excess Valence Z	(Q solvent - Q impurity) Kcal.mole^{-1}			Goldschmidt Diameter A
					Experimental	Lazarus	Alfred & March	
Nickel	39	2.7	56.5	-1	-9.4	-3.4	-4.7	2.49
Cobalt	60	5.7	55.2	-2	-8.1	-6.7	-12.4	2.50
Cobalt	39	1.9	54.1		-7.0			
Iron	39	1.4	51.8	-3	-4.7	-10.1	-23.6	2.52
Copper	16	0.47	47.1	0	-	-	-	2.55
Zinc	61	0.34	45.6	+1	+1.5	+3.4	+2.6	2.75
Cadmium	62	0.93	45.7	+1	+1.4	+3.4	+2.6	3.04
Antimony	—	0.34	42.0	+4	+5.1	+13.4	+7.4	3.23

TABLE 7

Temperature °C.	D uncorrected $cm.^2/sec.^{-1}$	Expansion Correction	Strain Correction	D Corrected $cm.^2\ sec.^{-1}$	Total Strain %	Strain Rate $sec.^{-1}$	D Experimental / D Calculated from Mechanical Sectioning.
633	$2.6.10^{-11}$	1.024	-	$2.66 \pm 0.3.10^{-11}$	-	-	-
567	$3.4.10^{-12}$	1.02	-	$3.47 \pm 1.2.10^{-12}$	-	-	-
540	$6.2.10^{-13}$	1.02	-	$6.30 \pm 1.2.10^{-13}$	-	-	-
594	$4.90.10^{-12}$	1.022	1.08	$5.4 \pm 0.4.10^{-12}$	8	3.10^{-6}	.6
598	$6.33.10^{-12}$	1.022	1.10	$7.0 \pm 0.4.10^{-12}$	10	4.10^{-6}	.7
594	$2.04.10^{-11}$	1.022	1.15	$2.4 \pm 0.2.10^{-11}$	29	2.10^{-5}	2.5

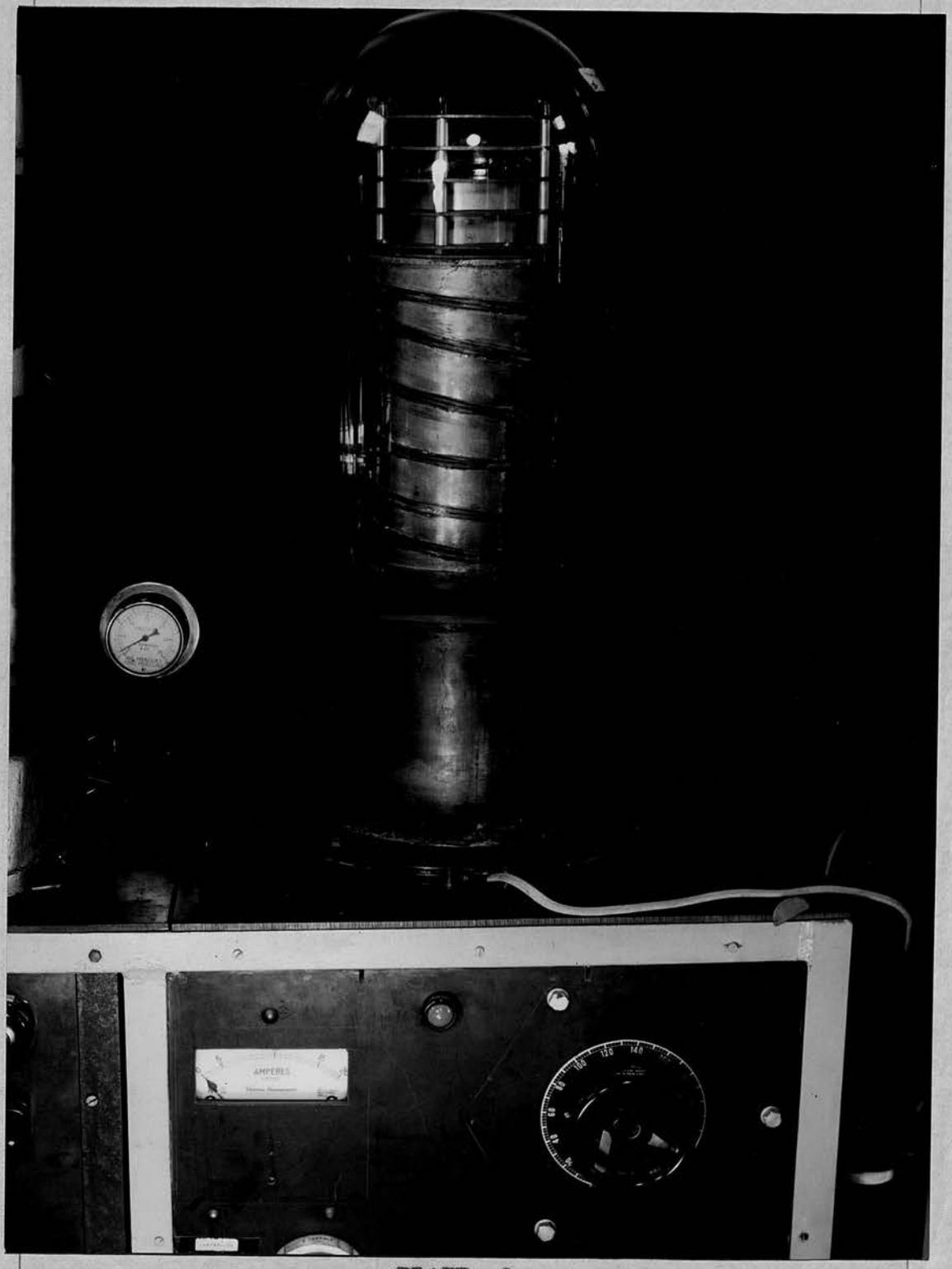


PLATE 1.

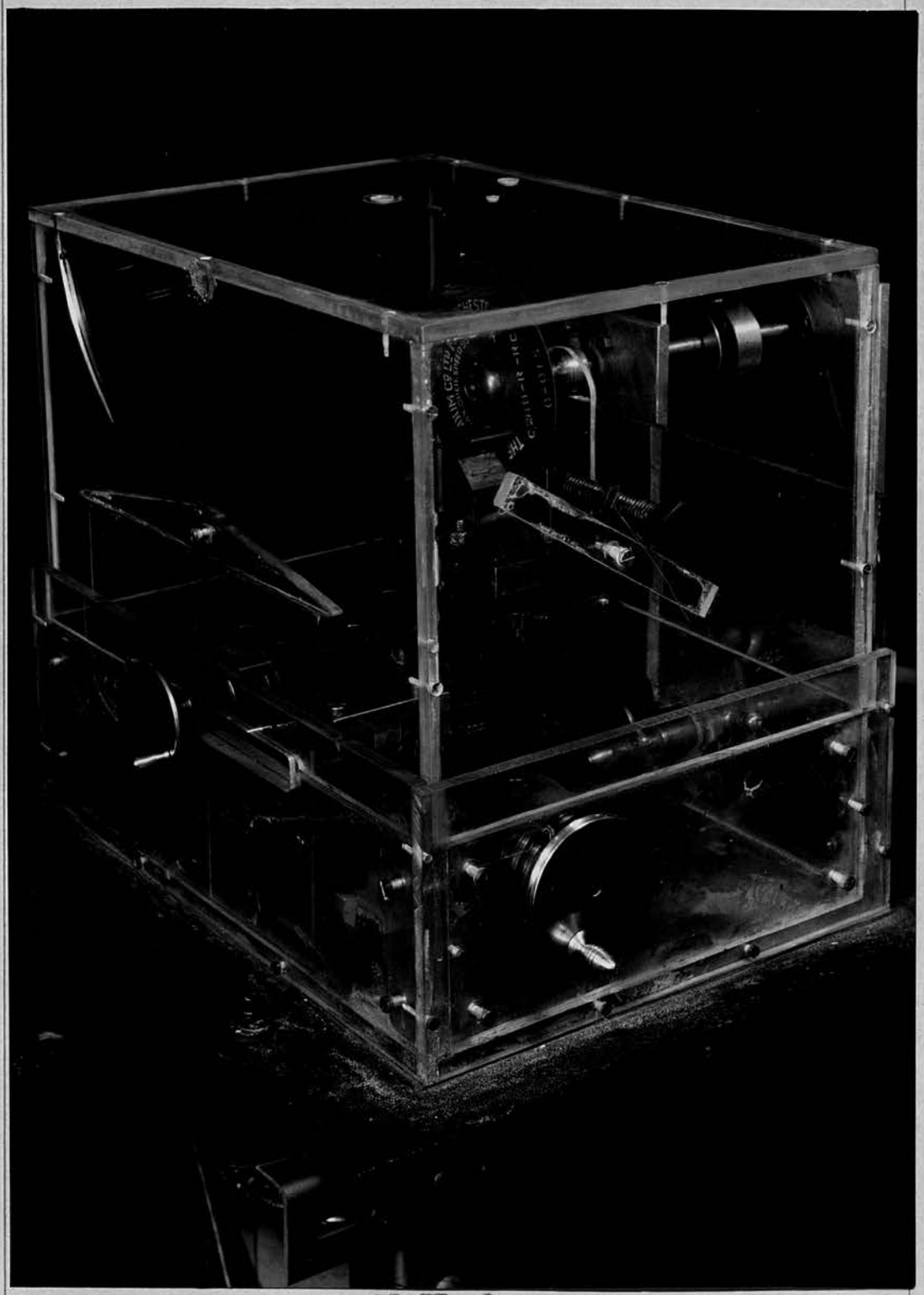


PLATE 2.

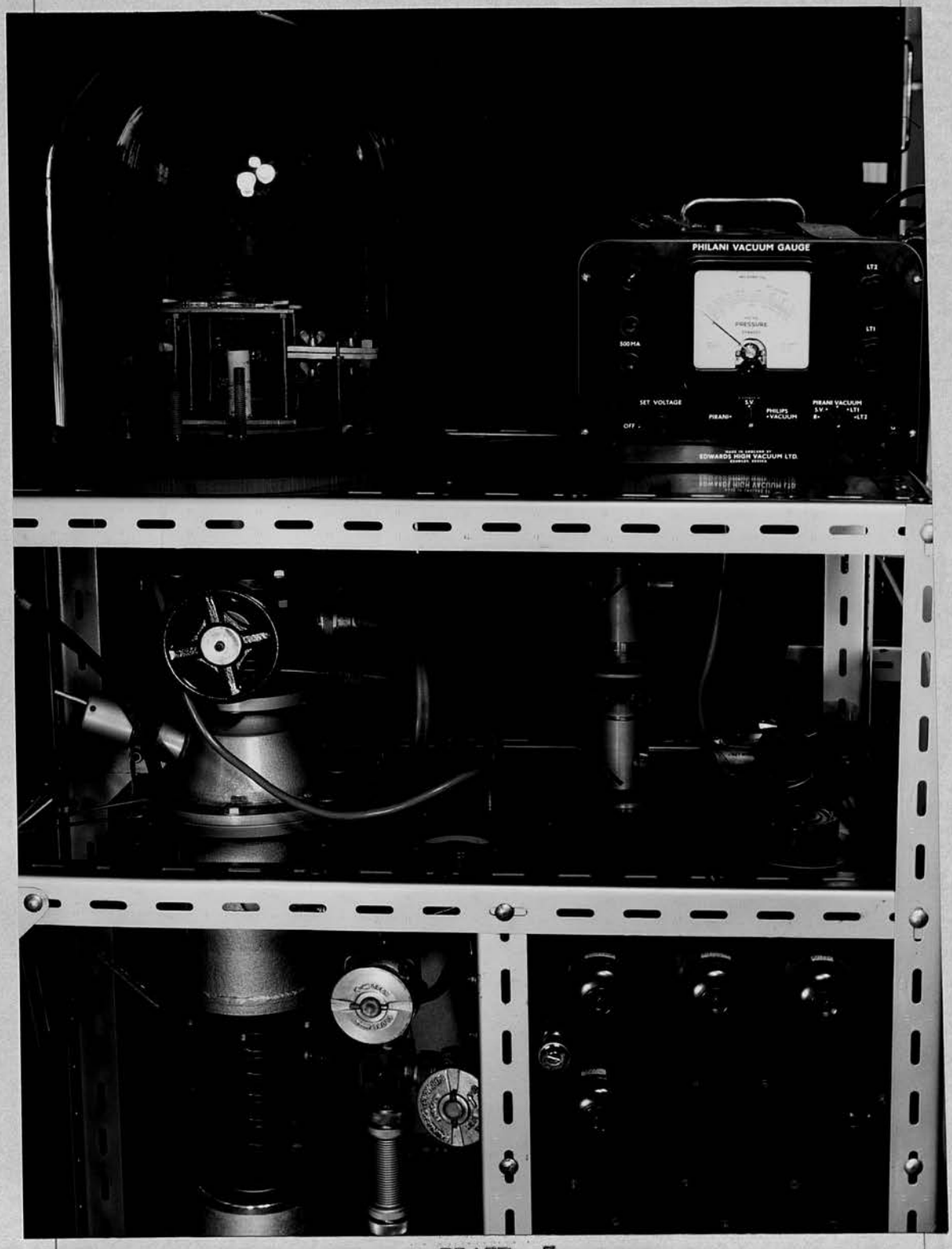
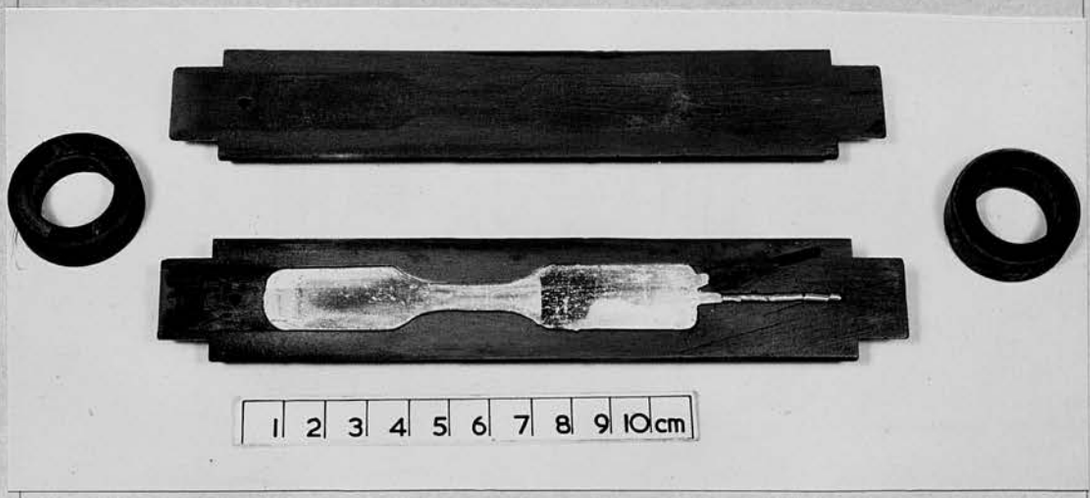

PHILANI VACUUM GAUGE
PRESSURE
500 MA
SET VOLTAGE
OFF
PIRANI+
5V
PHILIPS
+VACUUM
PIRANI VACUUM
5V +
8+
+LT1
+LT2
LT2
LT1
EDWARDS HIGH VACUUM LTD.

PLATE 3.



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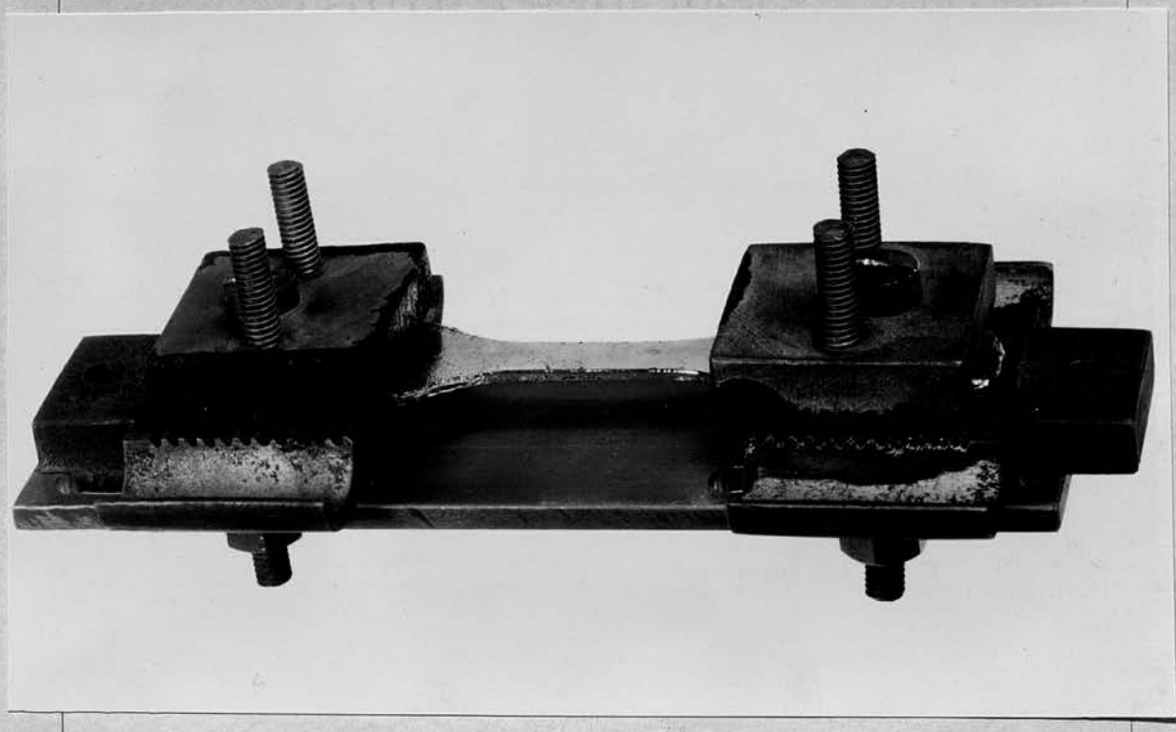

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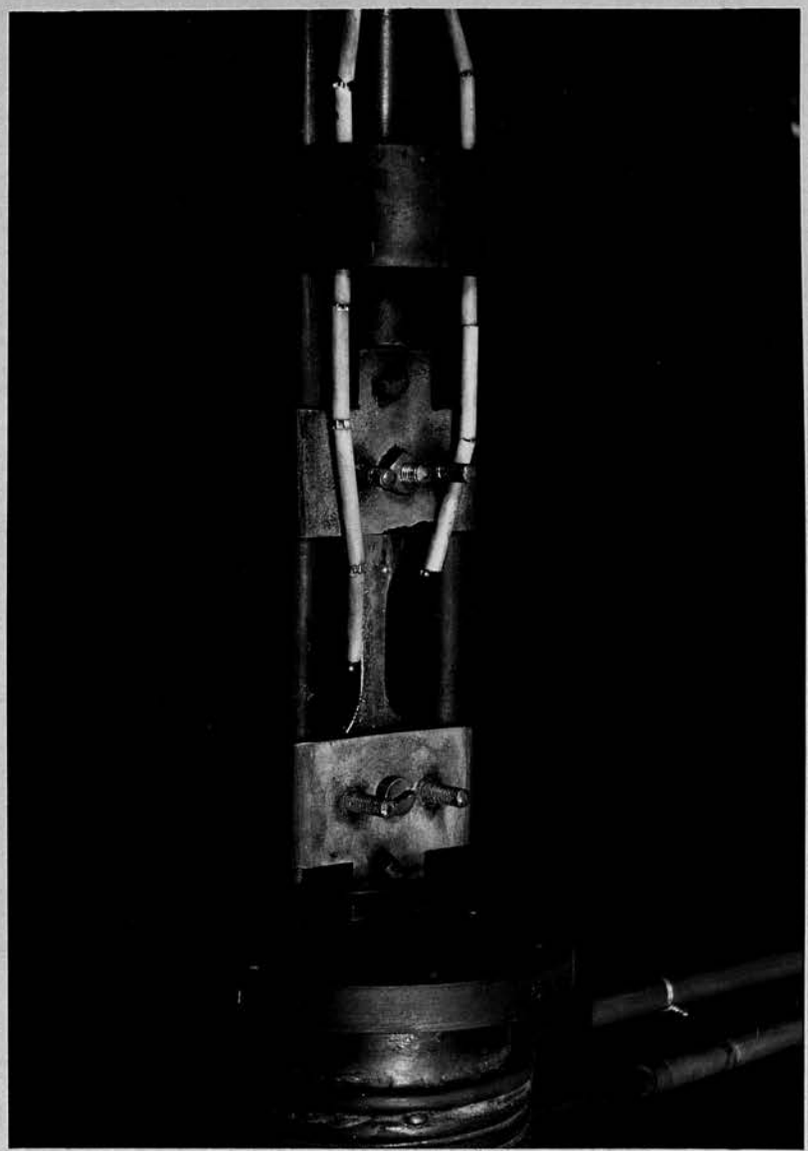

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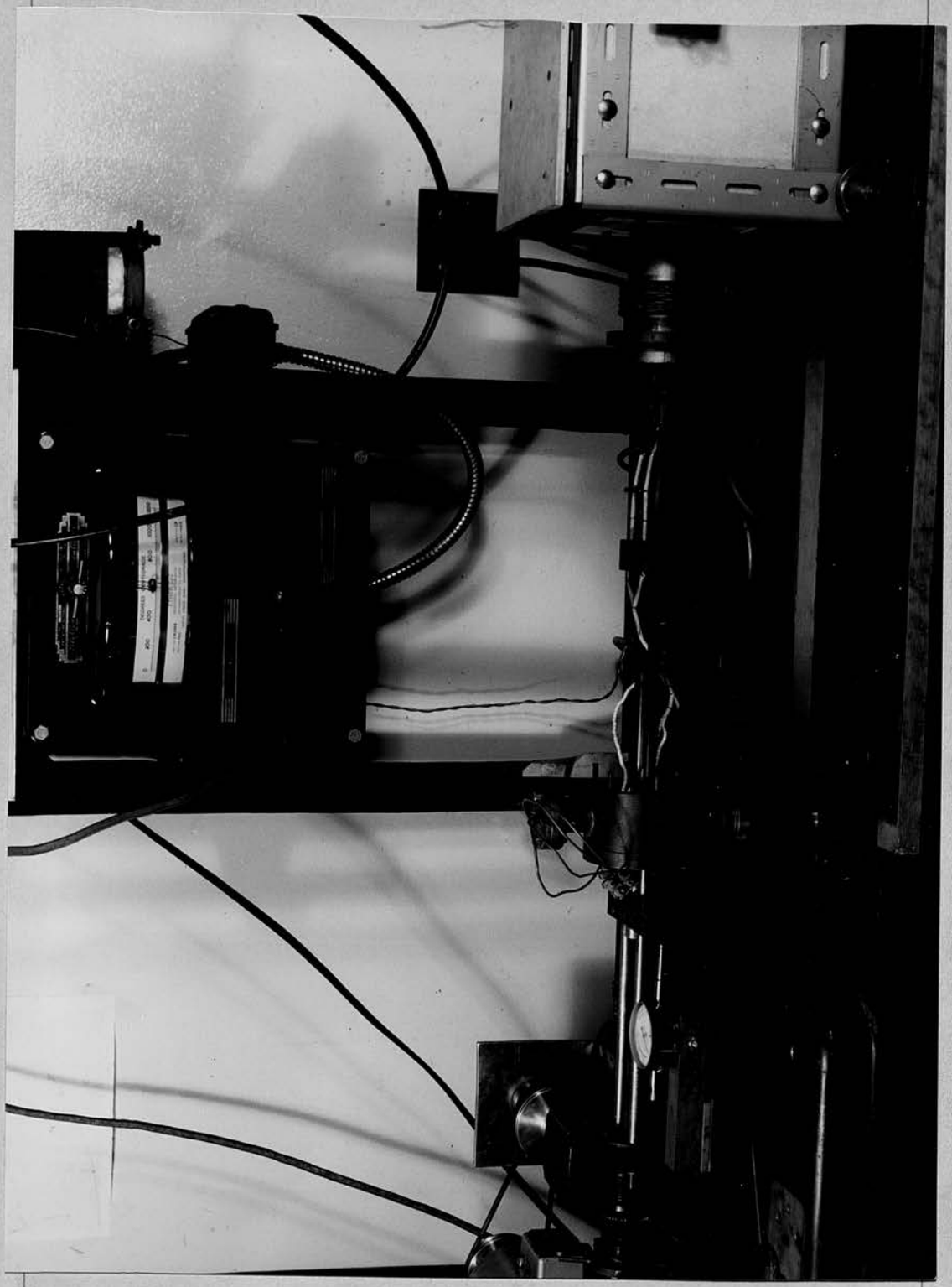
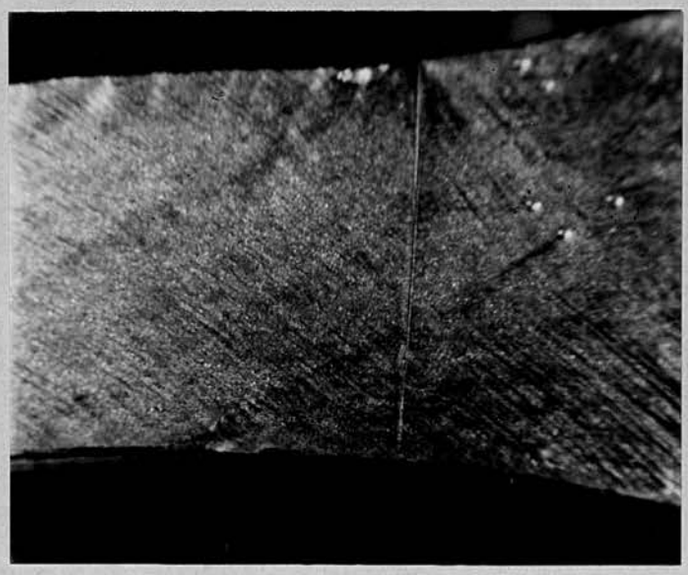


PLATE 7.



(x 10)

PLATE 8.

(x 200)

PLATE 9.

(x 200)

PLATE 10.

(x 200)

PLATE 11.

SPECIMEN HOLDER

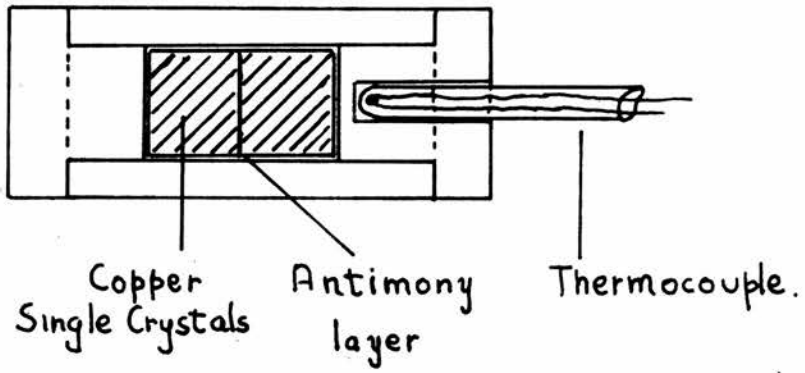
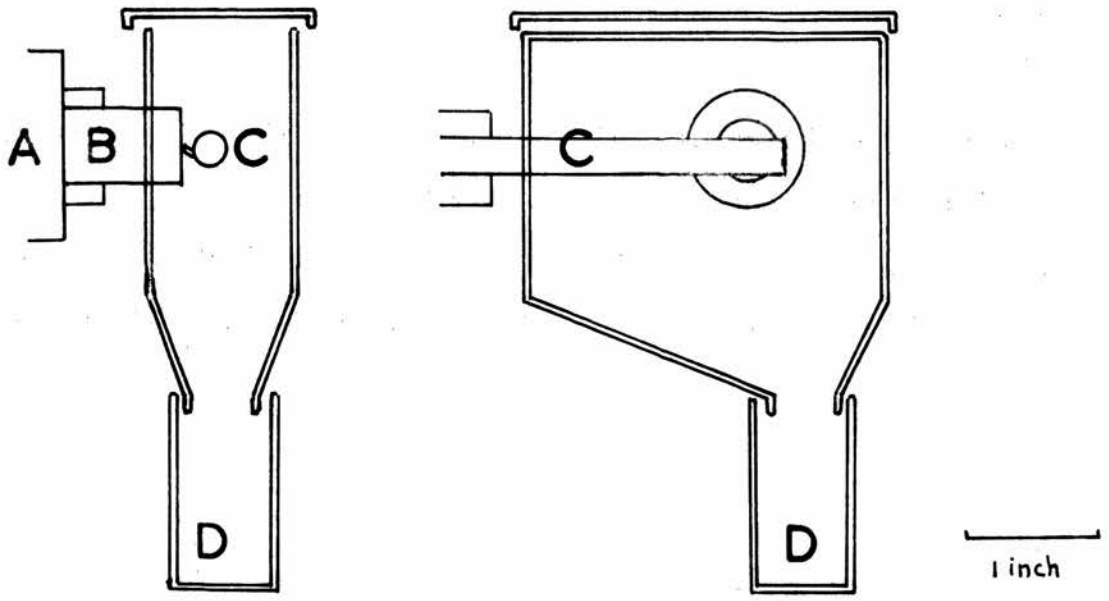


FIGURE 2.

PERSPEX COLLECTING BOX



A LATHE CHUCK
B DIFFUSION SPECIMEN
C CUTTING TOOL
D WEIGHING BOTTLE

FIGURE 3.

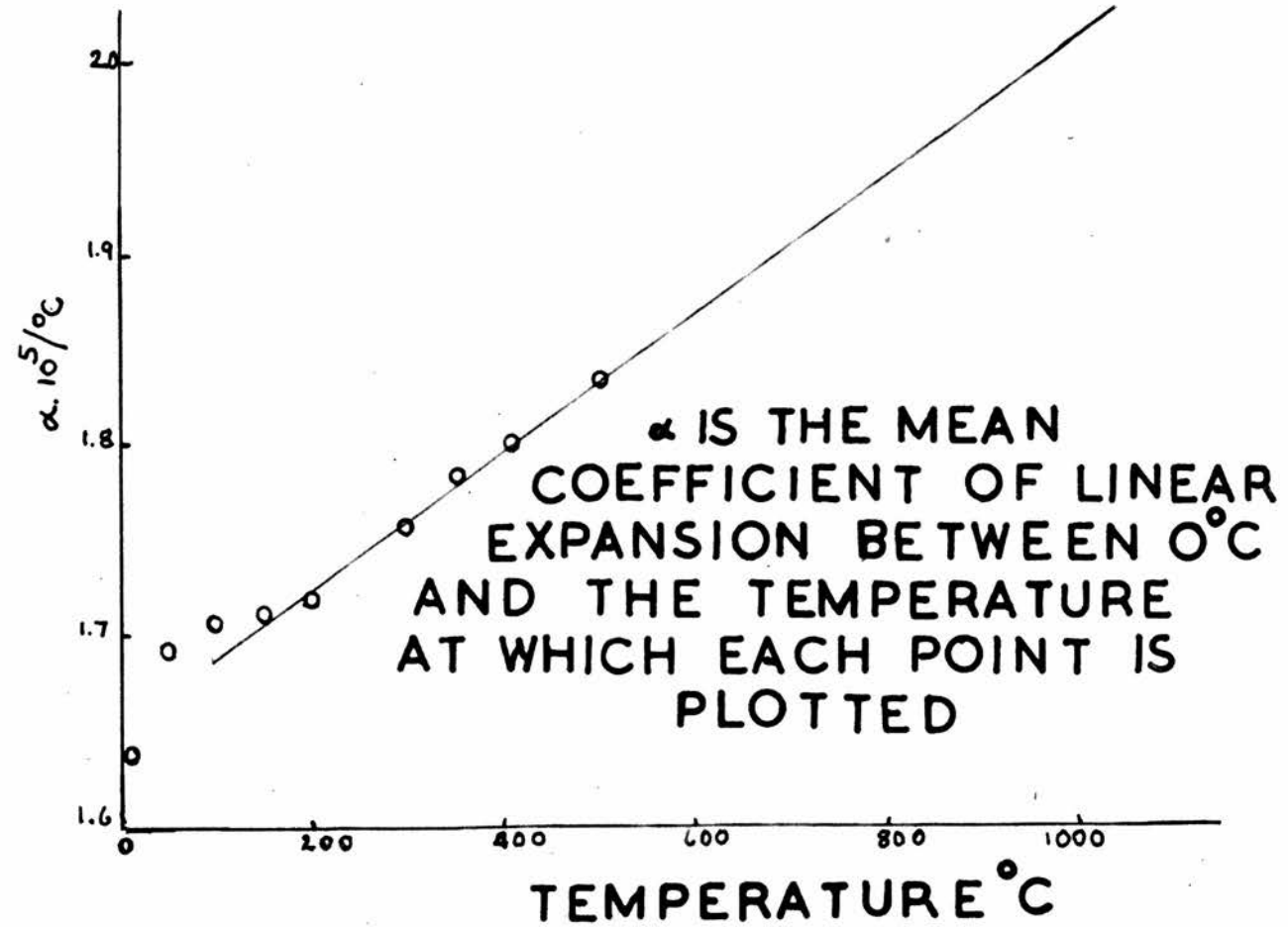
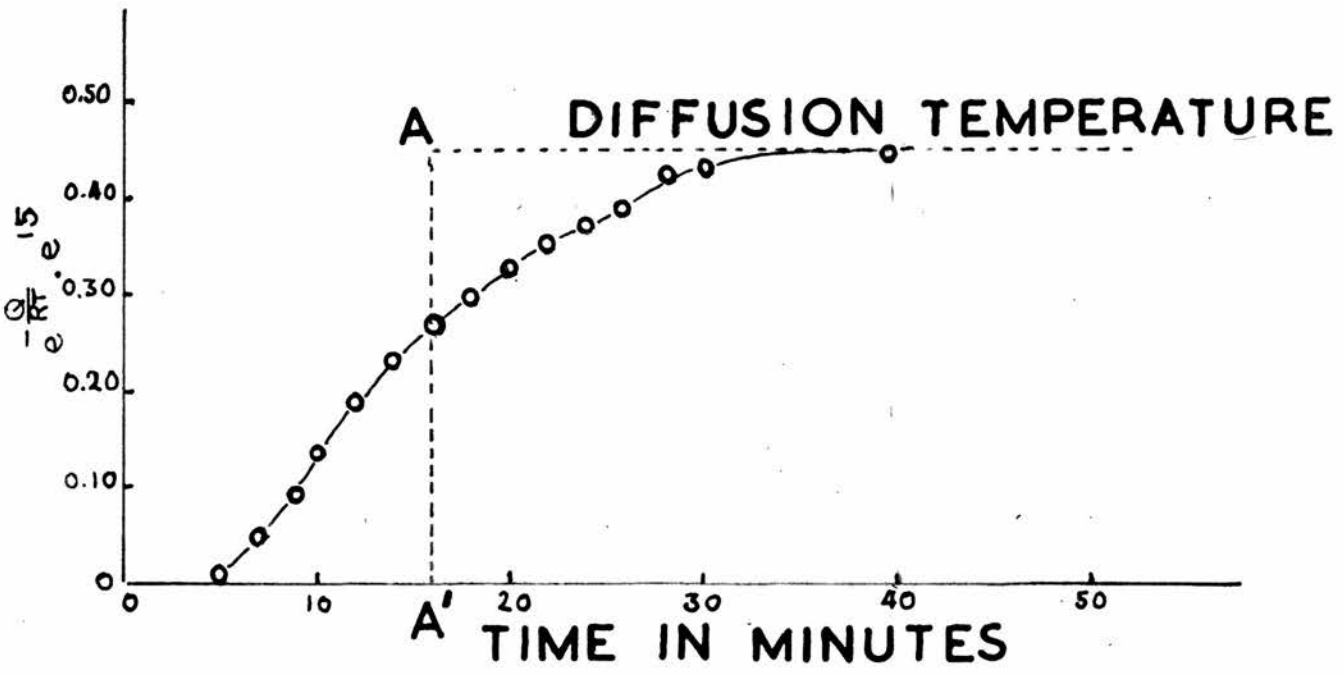


FIGURE 4.



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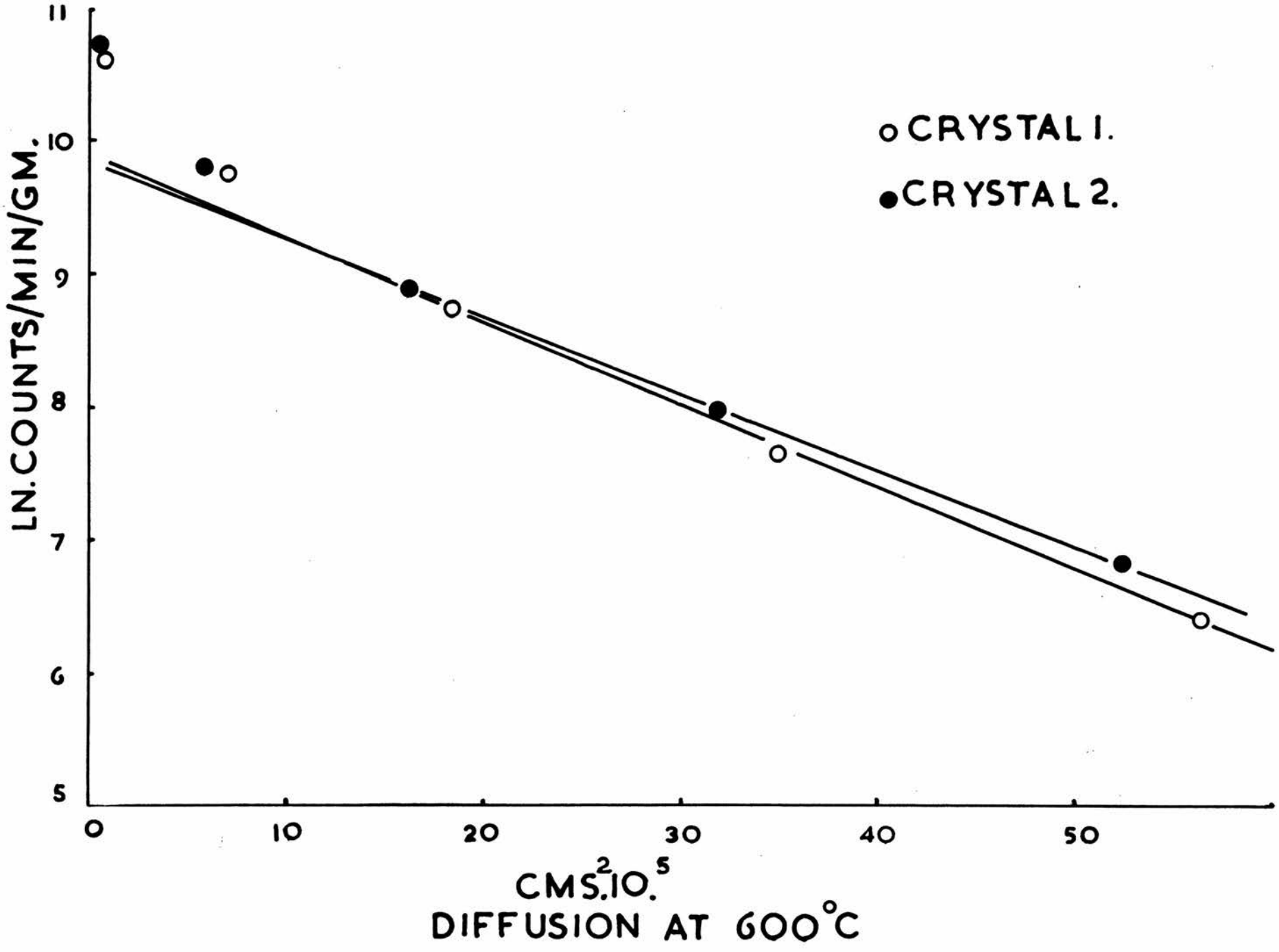

LN. COUNTS/MIN/GM.
11
10
9
8
7
6
5
0
10
20
30
40
50
CMS.^{2}10.^{5}
DIFFUSION AT 600°C
CRYSTAL 1.
CRYSTAL 2.

FIGURE 6.

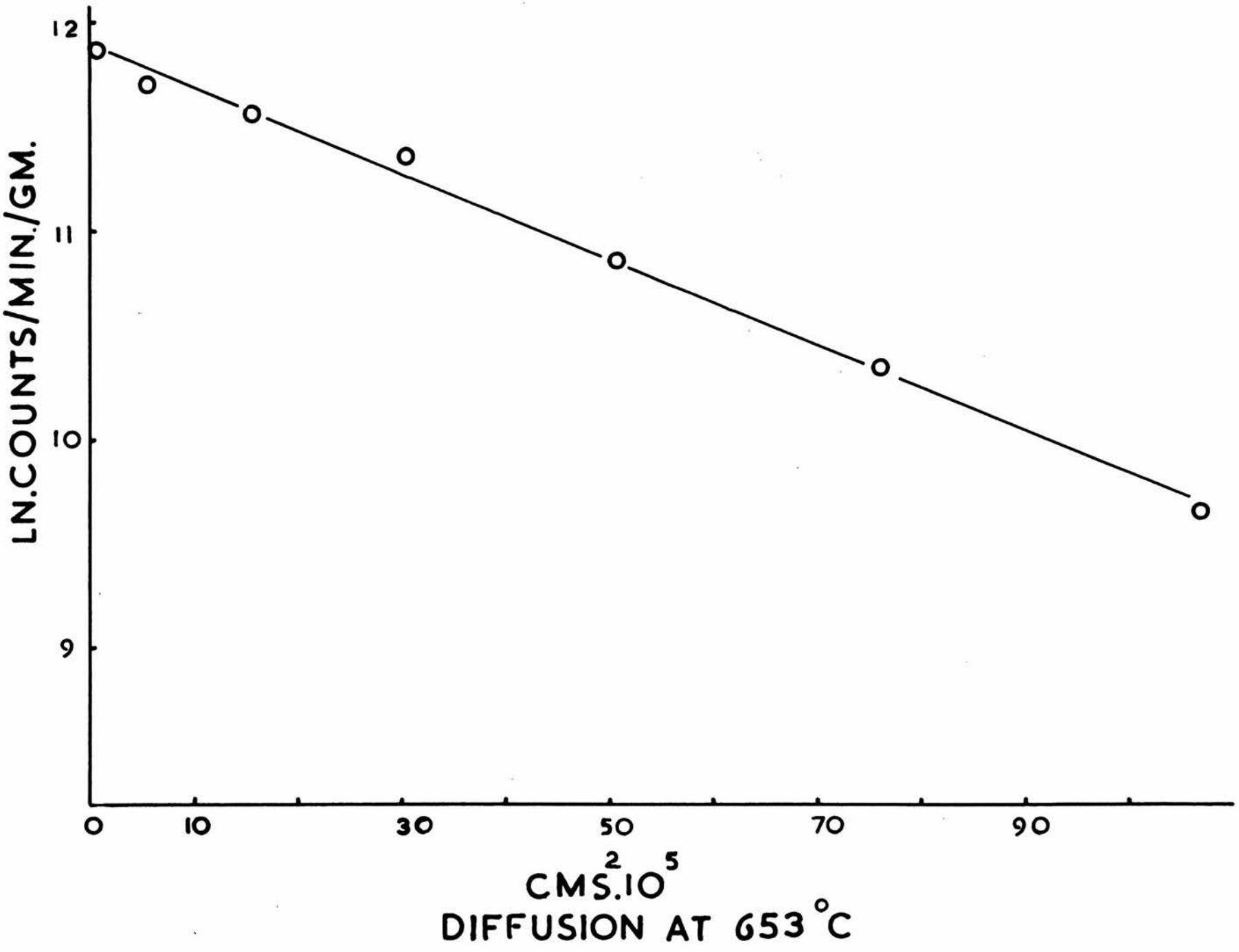

12
11
10
9
LN.COUNTS/MIN./GM.
0
10
30
50
70
90
CMS.10^2 5
DIFFUSION AT 653 °C

FIGURE 7.

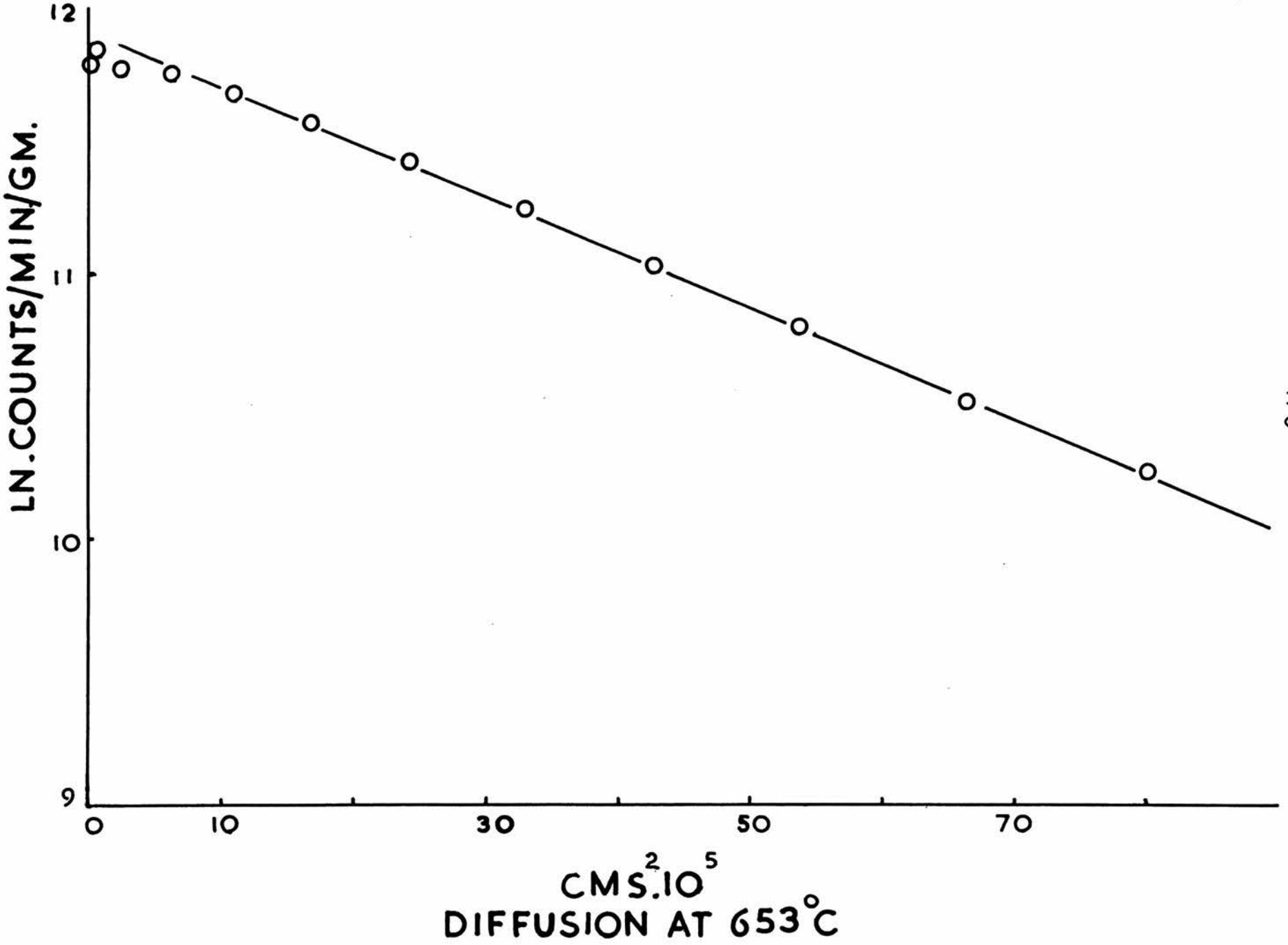

12
11
10
9
LN.COUNTS/MIN/GM.
0
10
30
50
70
CMS.10^2 5
DIFFUSION AT 653°C

FIGURE 8.

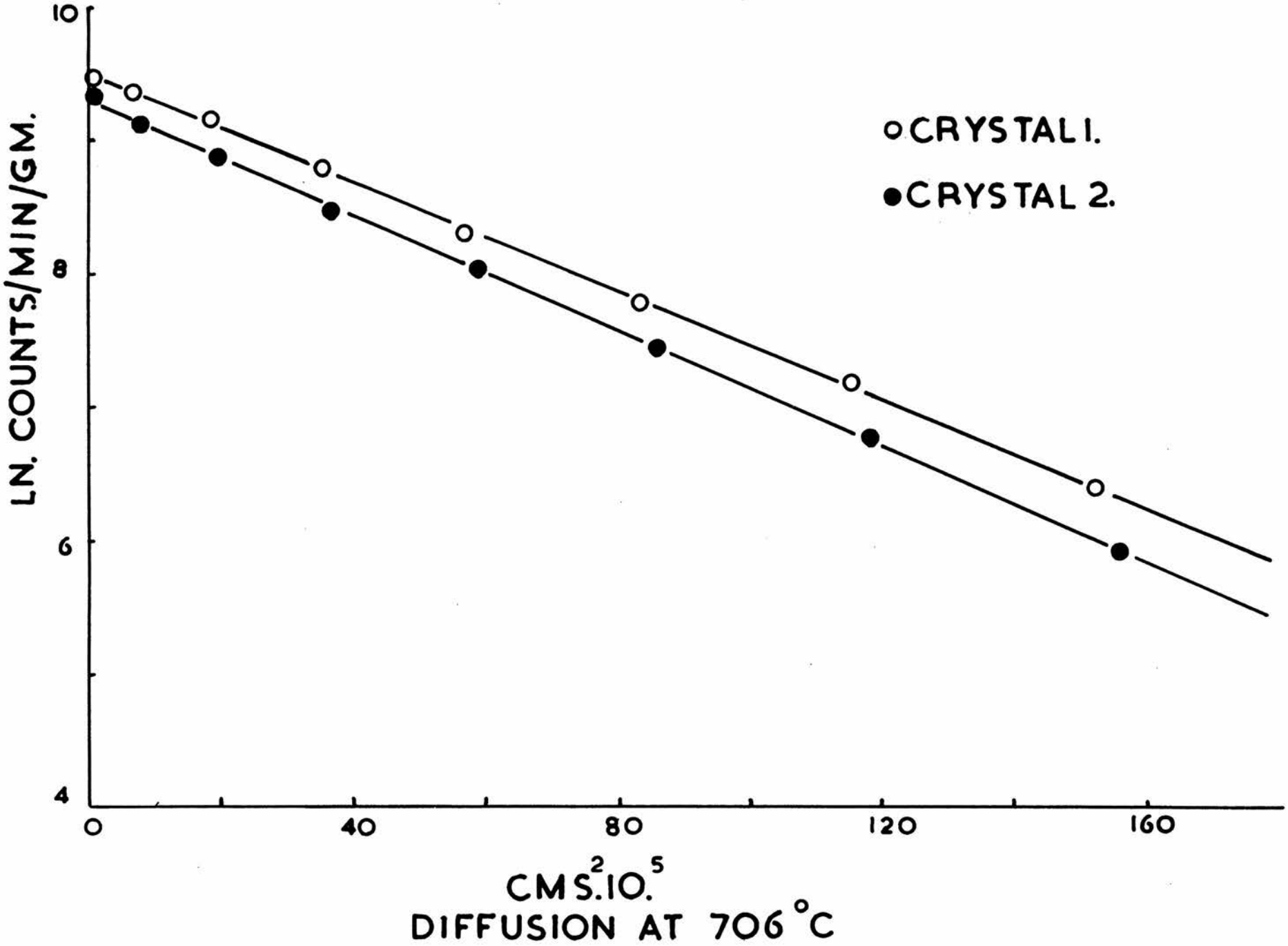

10
8
6
4
LN. COUNTS/MIN/GM.
CRYSTAL 1.
CRYSTAL 2.
0
40
80
120
160
CMS.^{2}10.^{5}
DIFFUSION AT 706 °C

FIGURE 9.

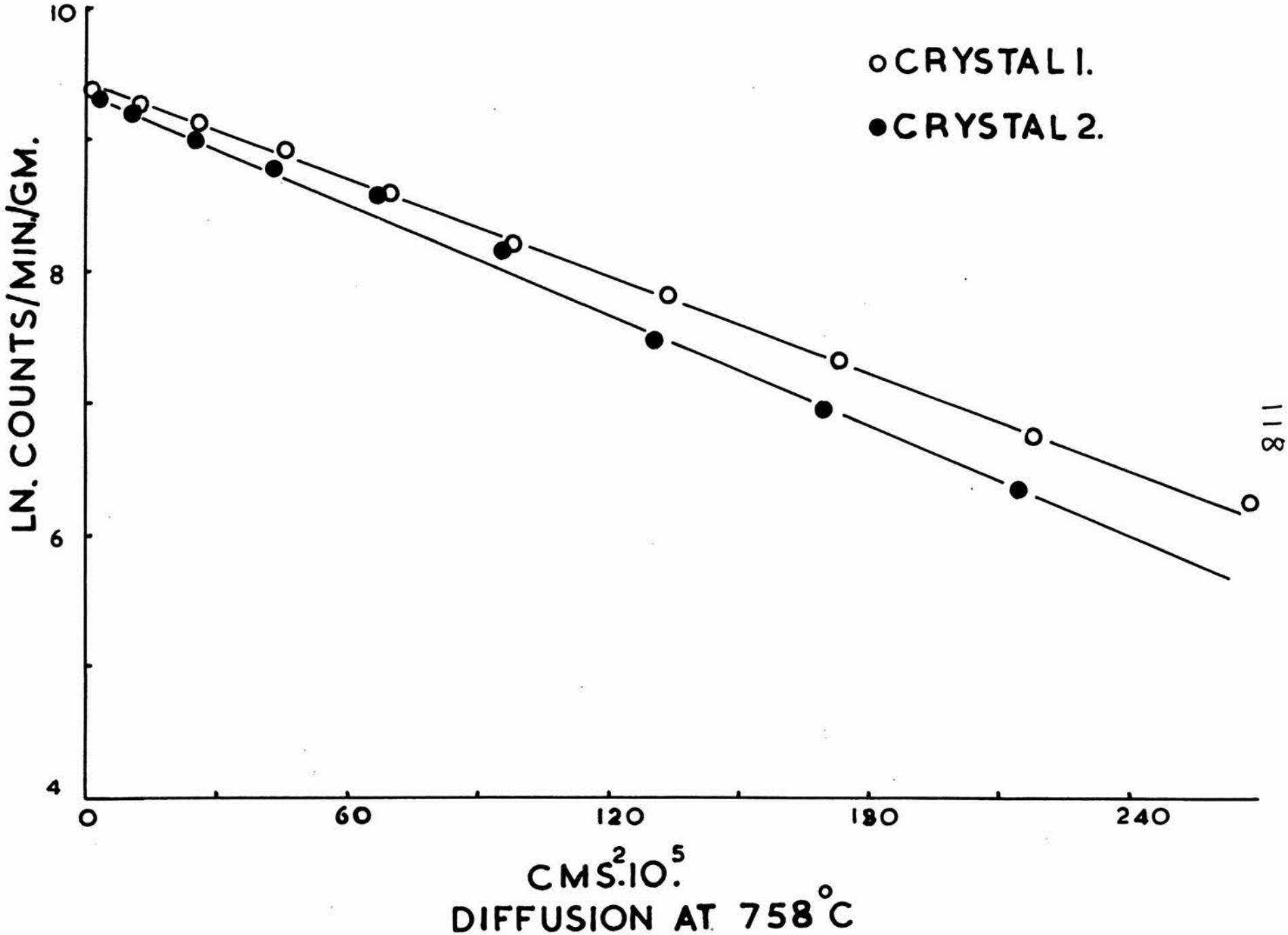

10
8
6
4
LN. COUNTS/MIN./GM.
o CRYSTAL 1.
● CRYSTAL 2.
0
60
120
180
240
$CMS^2.10^5.$
DIFFUSION AT 758°C
118

FIGURE 10.

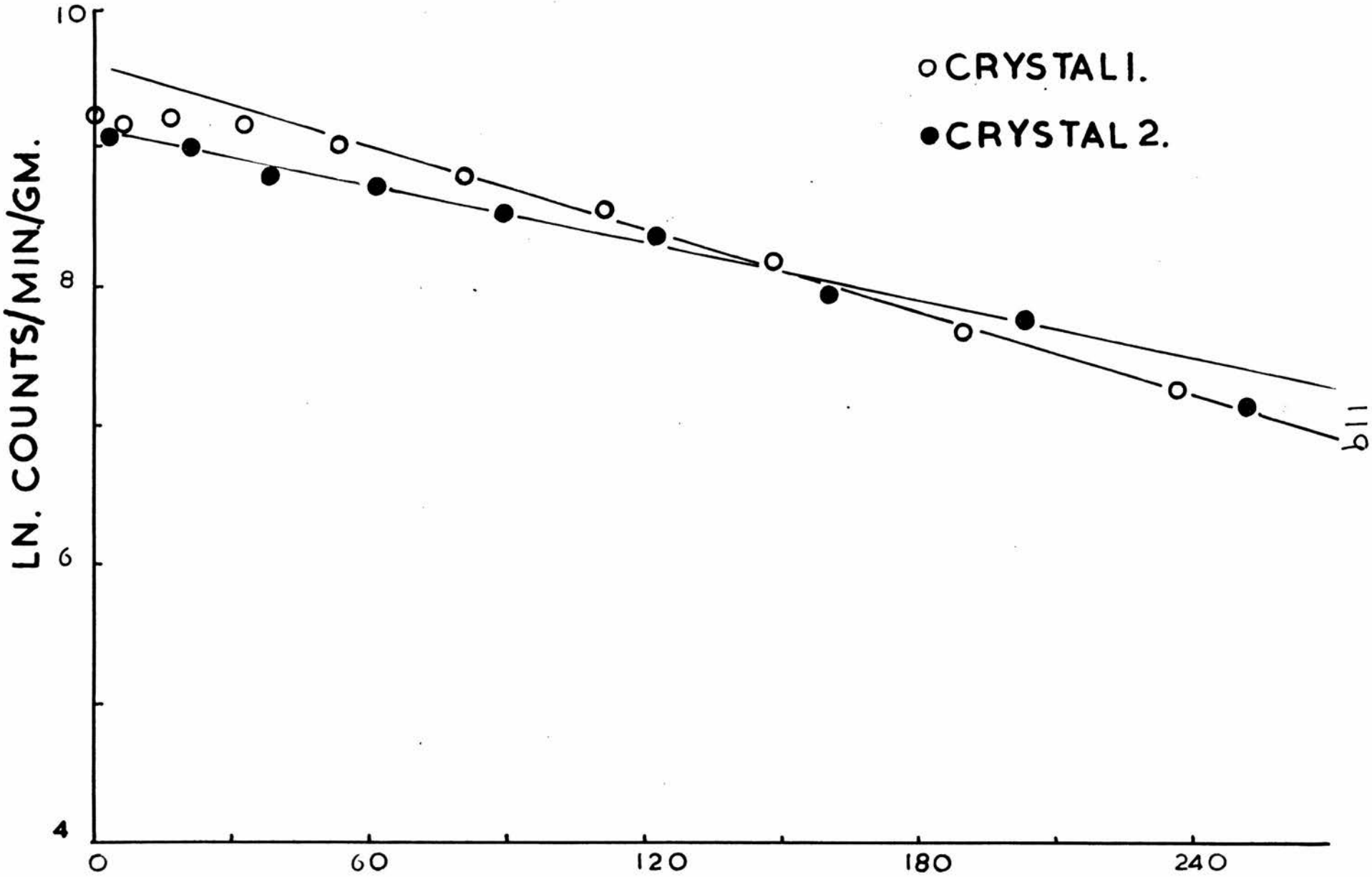

CRYSTAL 1.
CRYSTAL 2.
LN. COUNTS/MIN/GM.
10
8
6
4
0
60
120
180
240
CMS.^{2}.10.^{5}
DIFFUSION AT 806 °C
119

FIGURE 11.

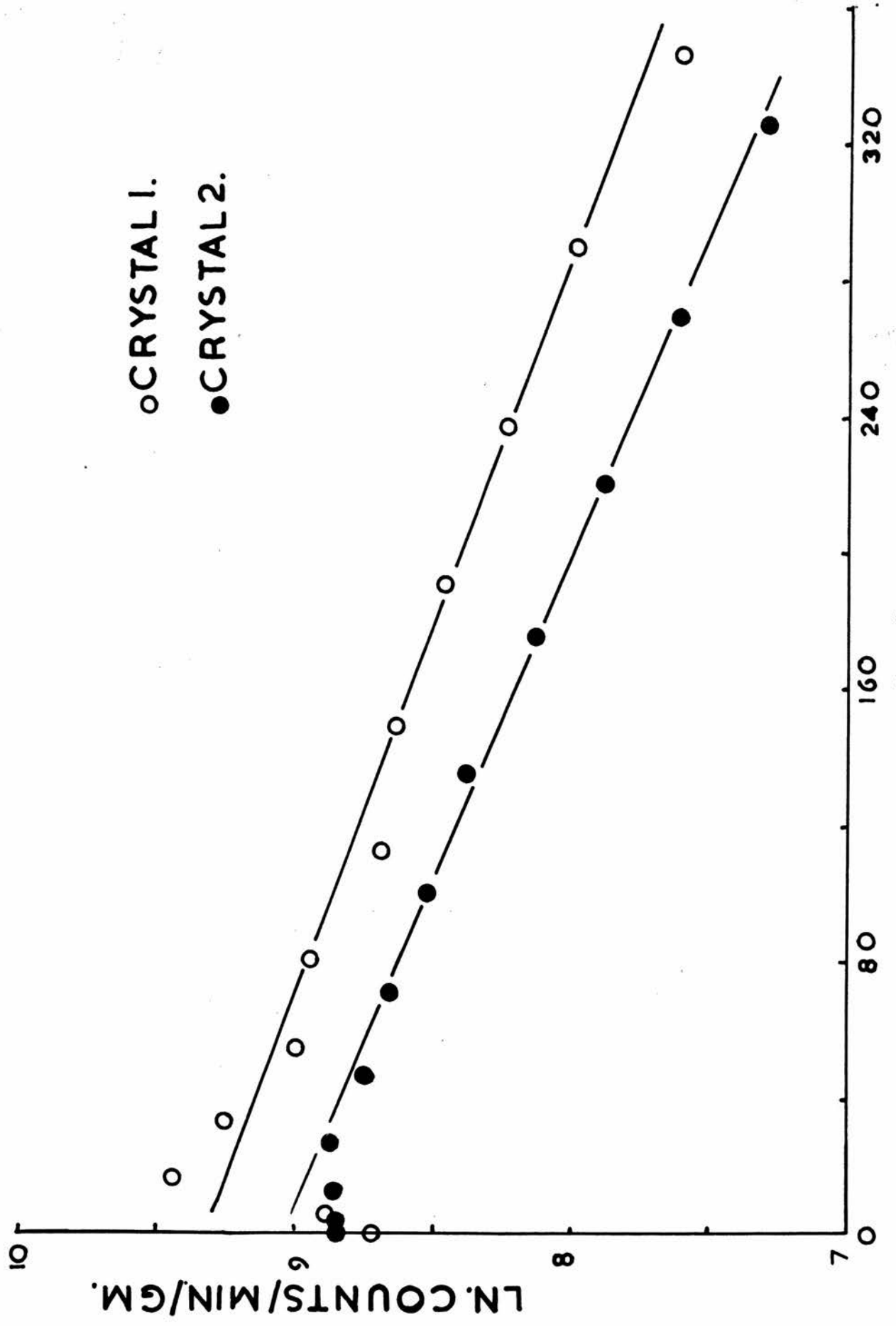

oCRYSTAL 1.
●CRYSTAL 2.
LN. COUNTS/MIN/GM.
10
9
8
7
0
80
160
240
320
CMS.^{2}.10.^{5}
DIFFUSION AT 859°C

FIGURE 12.

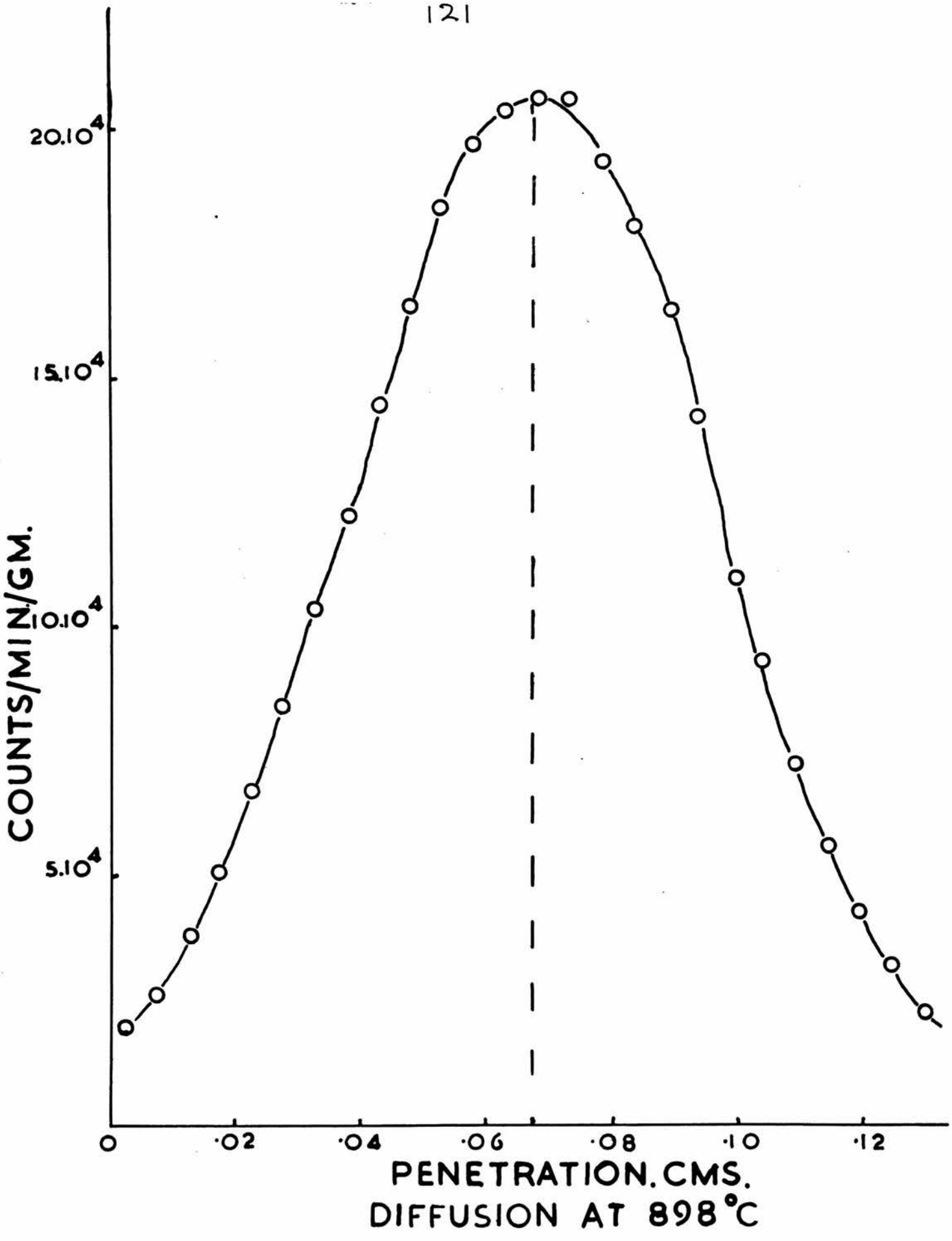

20.10⁴
15.10⁴
10.10⁴
5.10⁴
COUNTS/MIN./GM.
0
·02
·04
·06
·08
·10
·12
PENETRATION. CMS.
DIFFUSION AT 898°C

FIGURE 13.

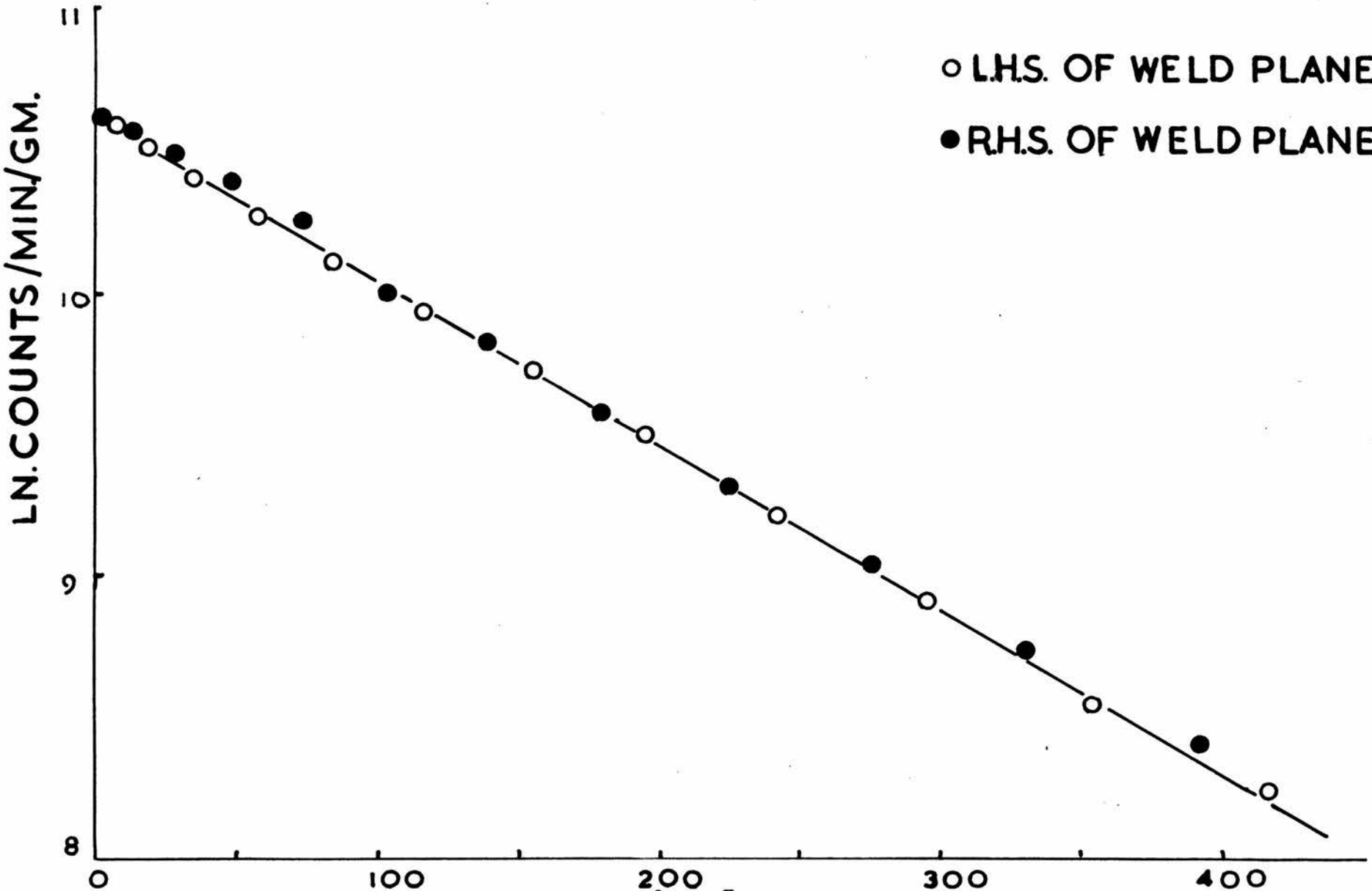

LN. COUNTS/MIN./GM.
11
10
9
8
0
100
200
300
400
CMS.^{2}10.^{5}
DIFFUSION AT 898°C
○ L.H.S. OF WELD PLANE
● R.H.S. OF WELD PLANE

FIGURE 14.

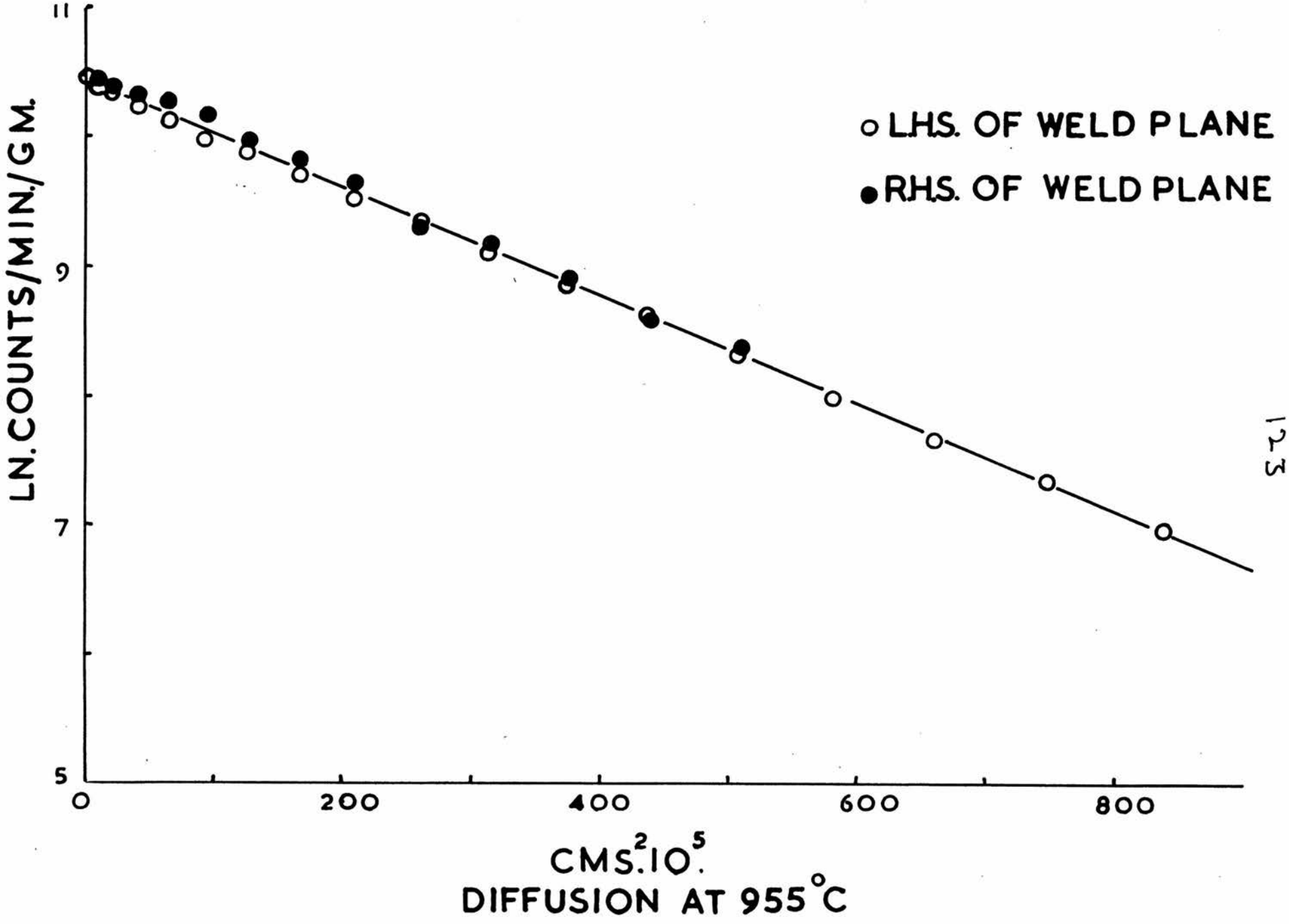

LN. COUNTS/MIN./GM.
11
9
7
5
0
200
400
600
800
○ L.H.S. OF WELD PLANE
● R.H.S. OF WELD PLANE
CMS.^{2}10^5.
DIFFUSION AT 955°C

FIGURE 15.

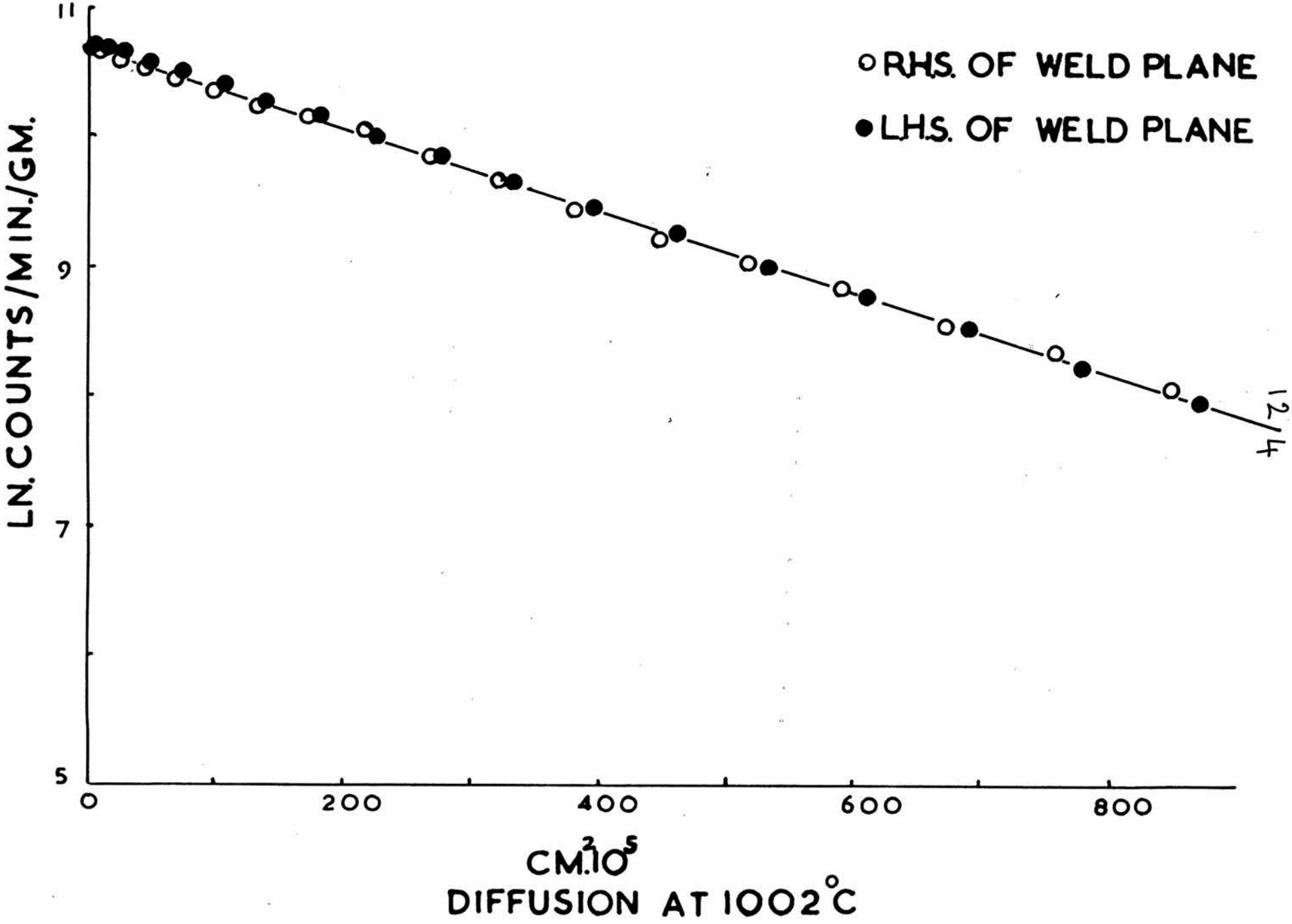
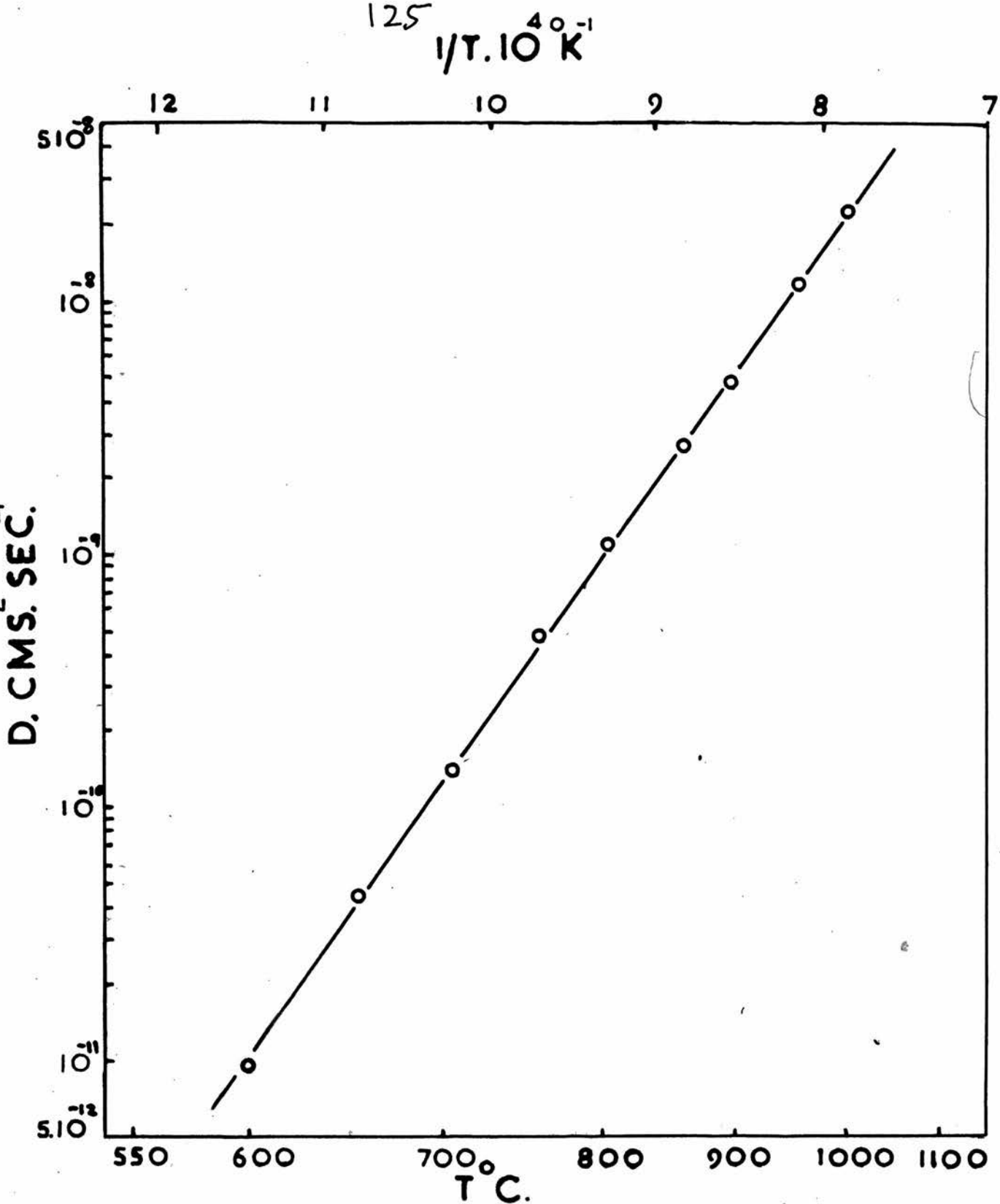

o R.H.S. OF WELD PLANE
● L.H.S. OF WELD PLANE
LN. COUNTS/MIN./GM.
11
9
7
5
0
200
400
600
800
12.4
CM.^{2}.10^5
DIFFUSION AT 1002°C

FIGURE 16



TEMPERATURE VARIATION OF THE DIFFUSION COEFFICIENT OF ANTIMONY IN COPPER.

FIGURE 17.

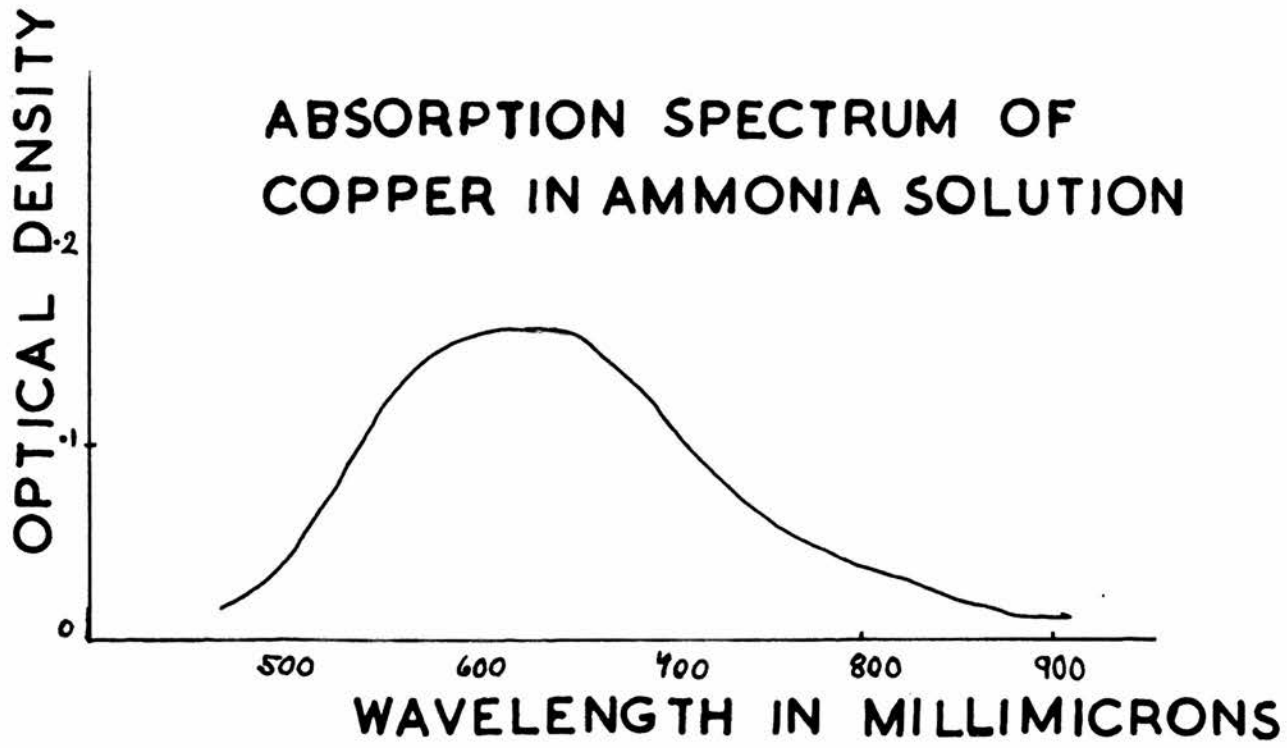


FIGURE 18

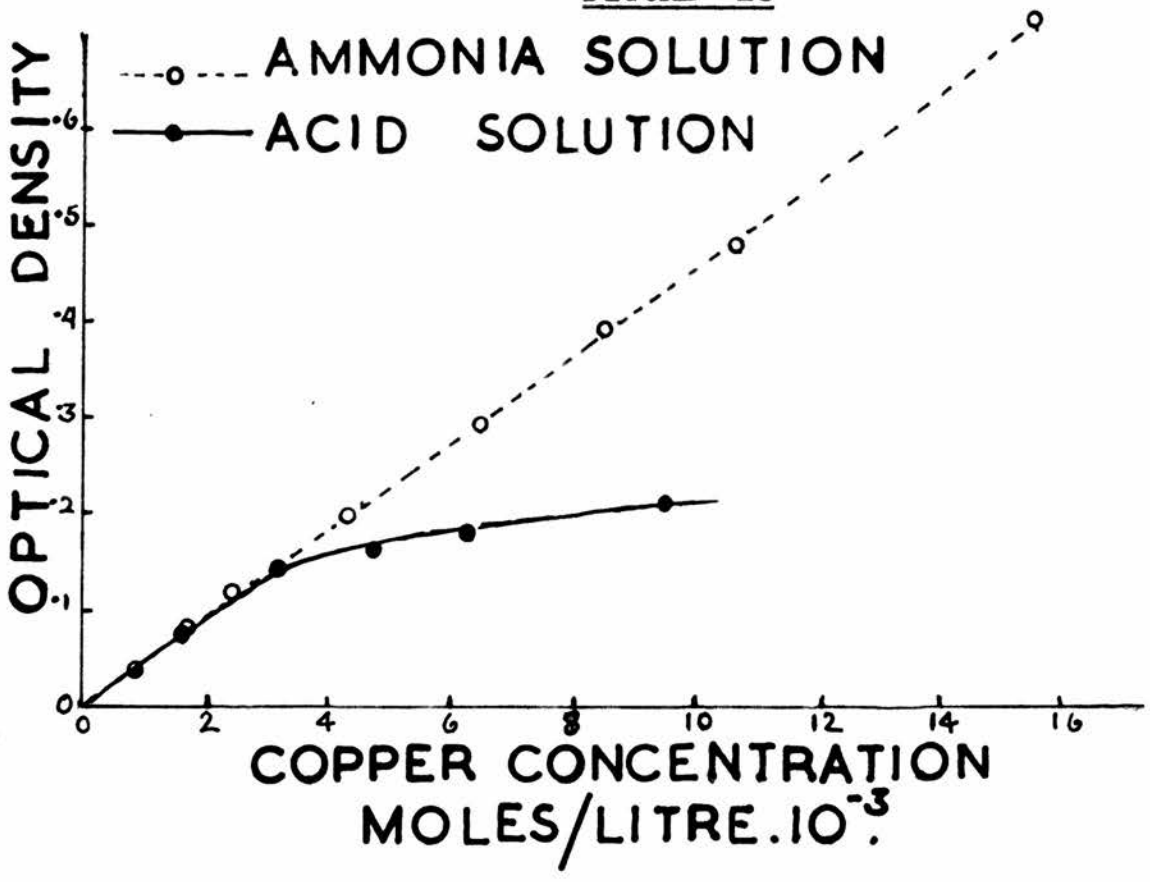


FIGURE 19.

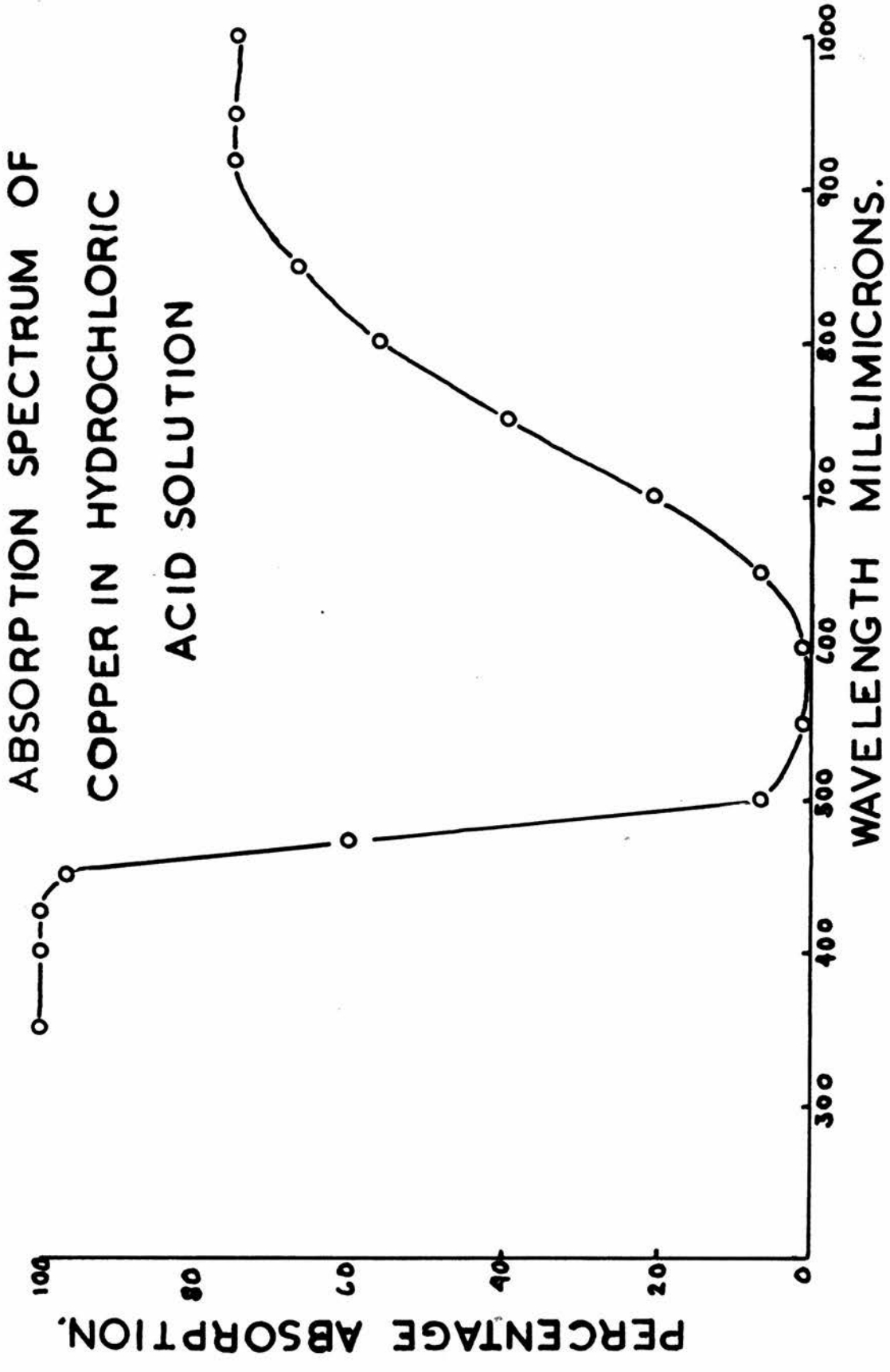

ABSORPTION SPECTRUM OF
COPPER IN HYDROCHLORIC
ACID SOLUTION
PERCENTAGE ABSORPTION.
0
20
40
60
80
100
300
400
500
600
700
800
900
1000
WAVELENGTH MILLIMICRONS.

FIGURE 20.

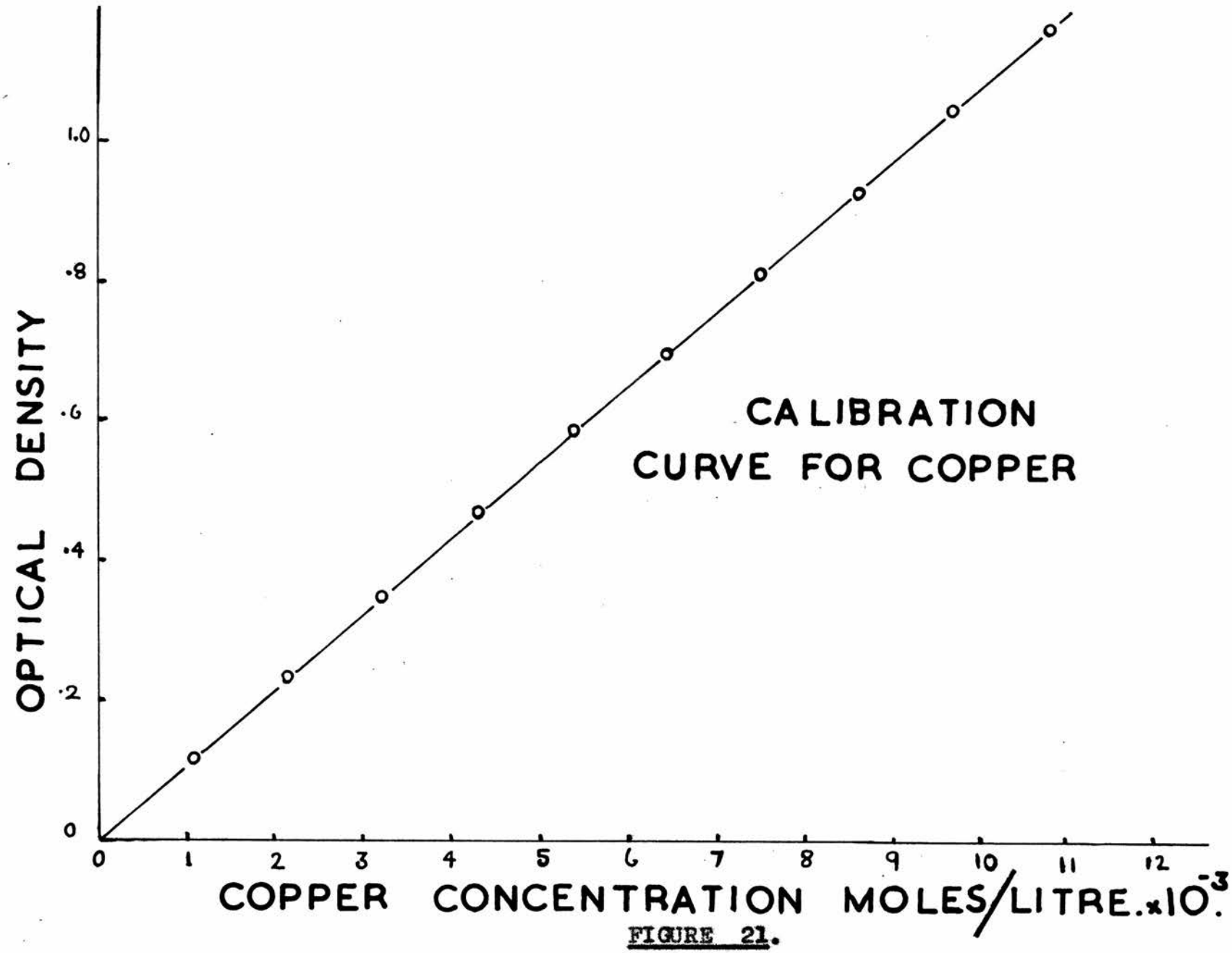
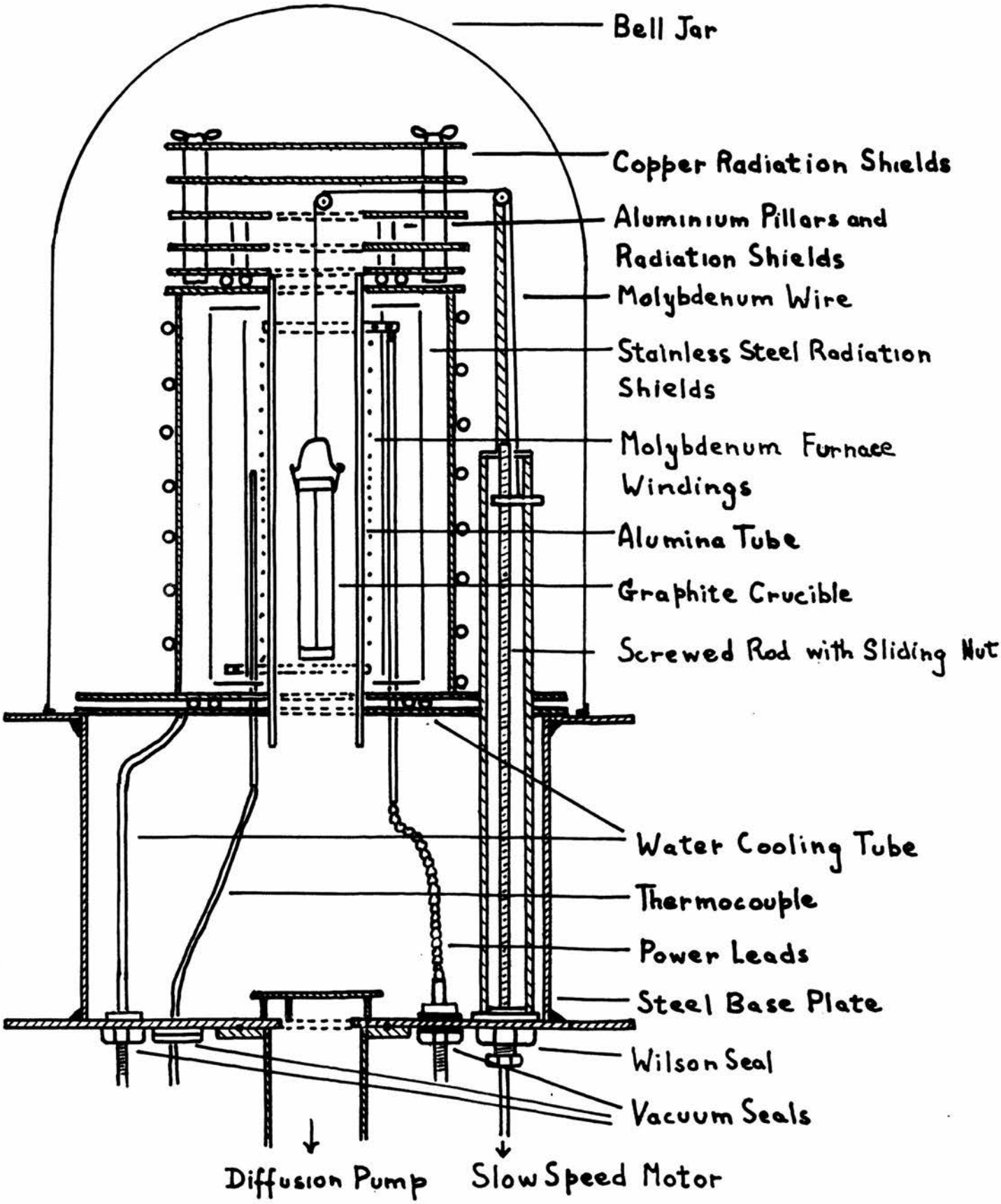
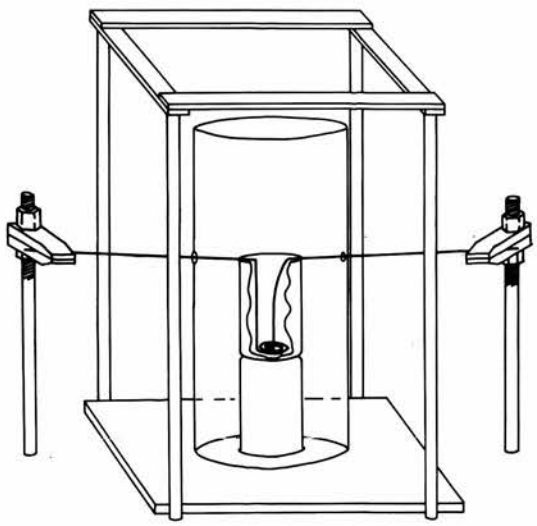

CALIBRATION
CURVE FOR COPPER
OPTICAL DENSITY
0
·2
·4
·6
·8
1·0
0 1 2 3 4 5 6 7 8 9 10 11 12
COPPER CONCENTRATION MOLES/LITRE.×10⁻³

FIGURE 21.



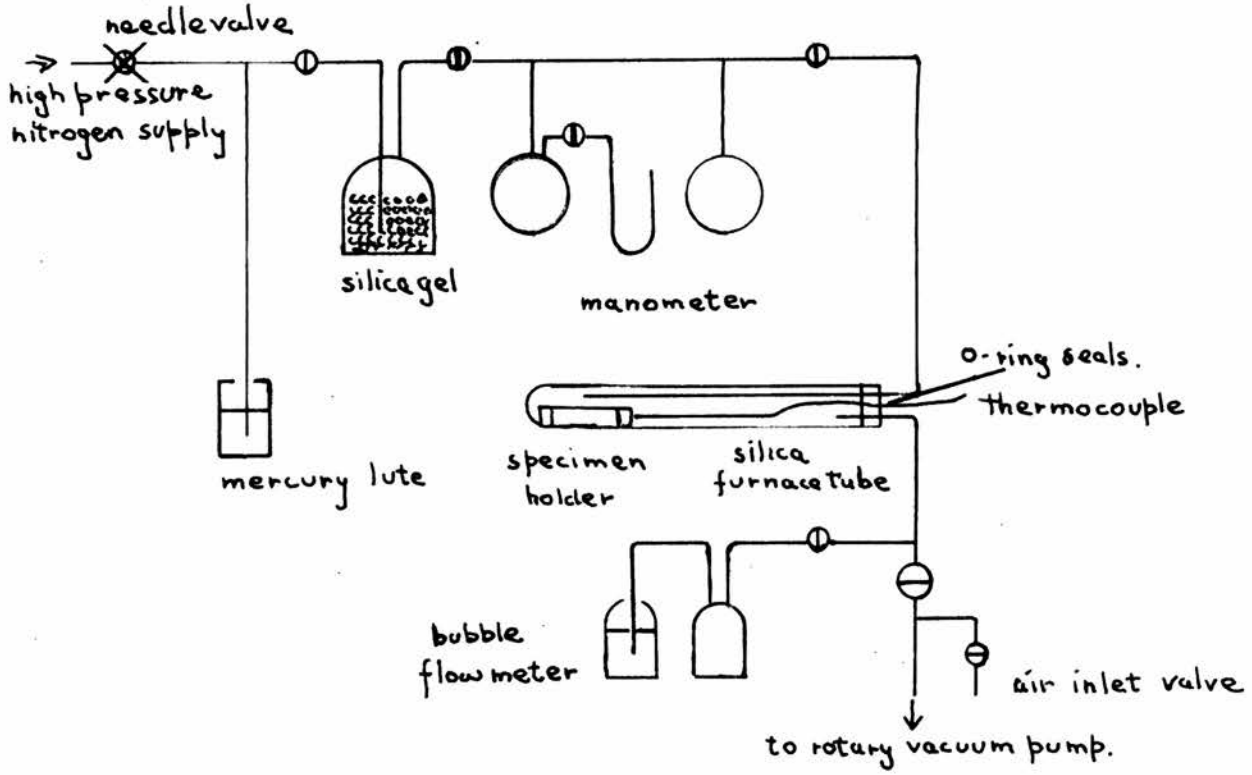
SINGLE CRYSTAL VACUUM FURNACE

FIGURE 22.



Active Evaporation Unit.

FIGURE 23.



CONTROLLED ATMOSPHERE FURNACE

FIGURE 24.

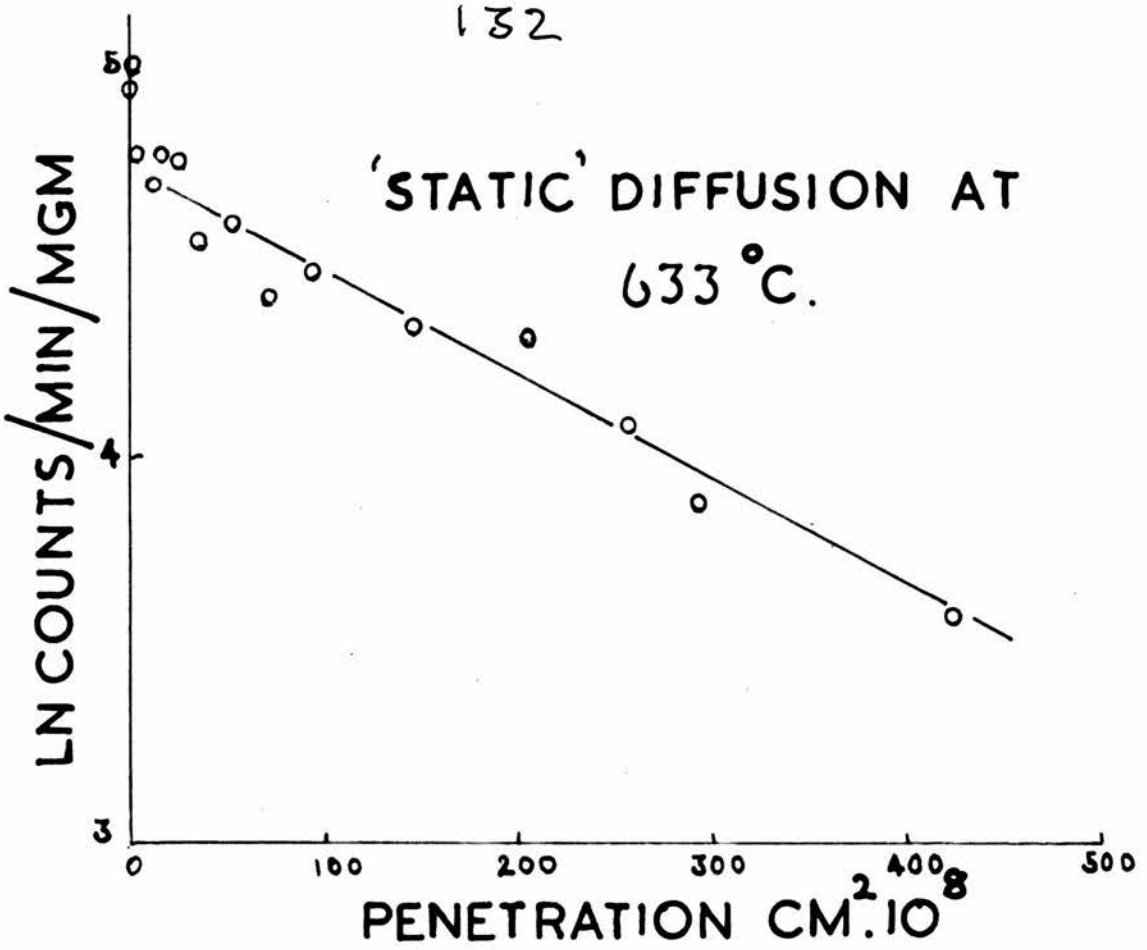


FIGURE 25.

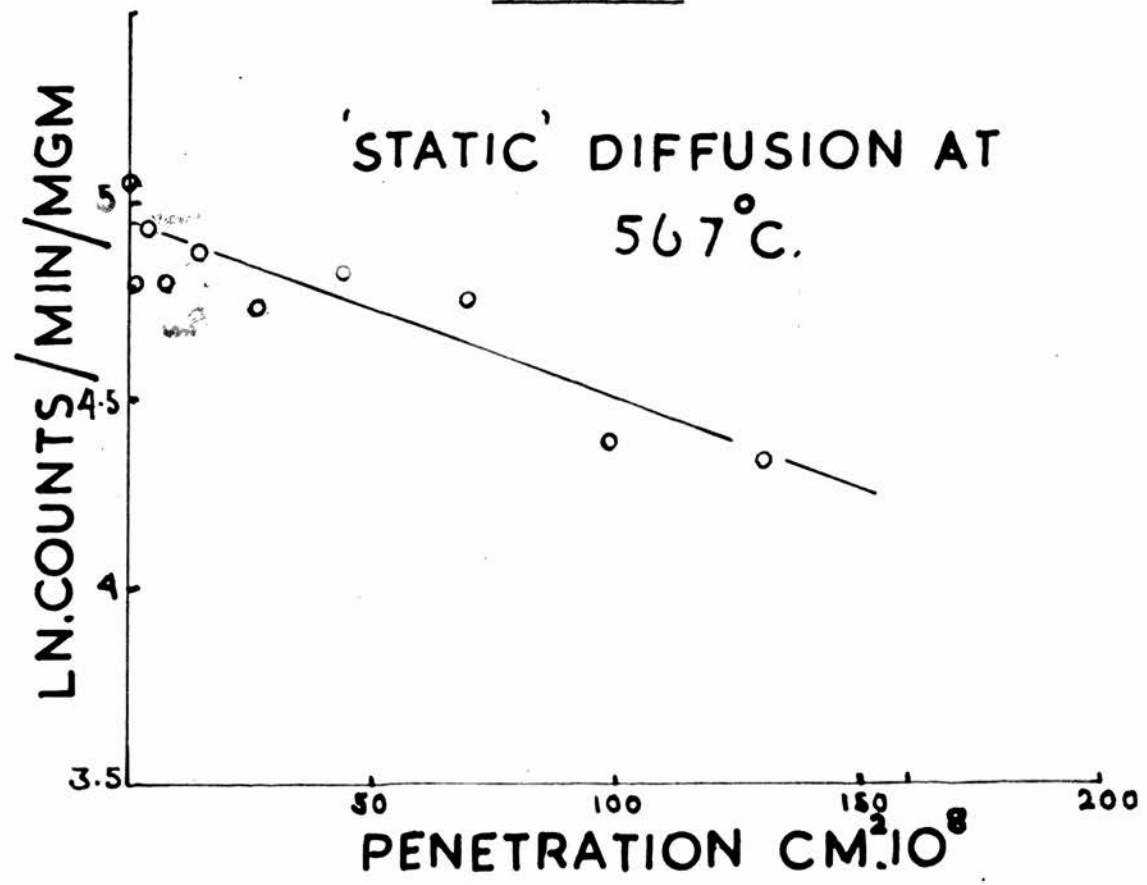


FIGURE 26.

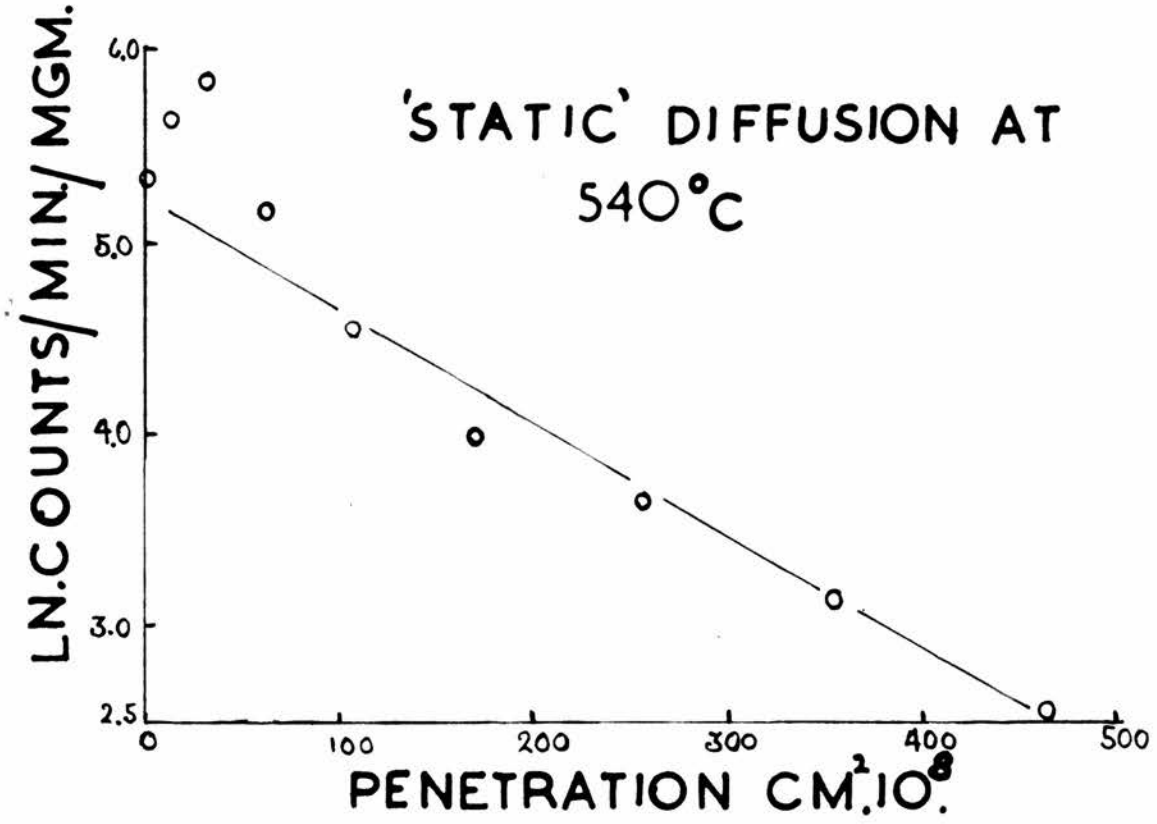


FIGURE 27.

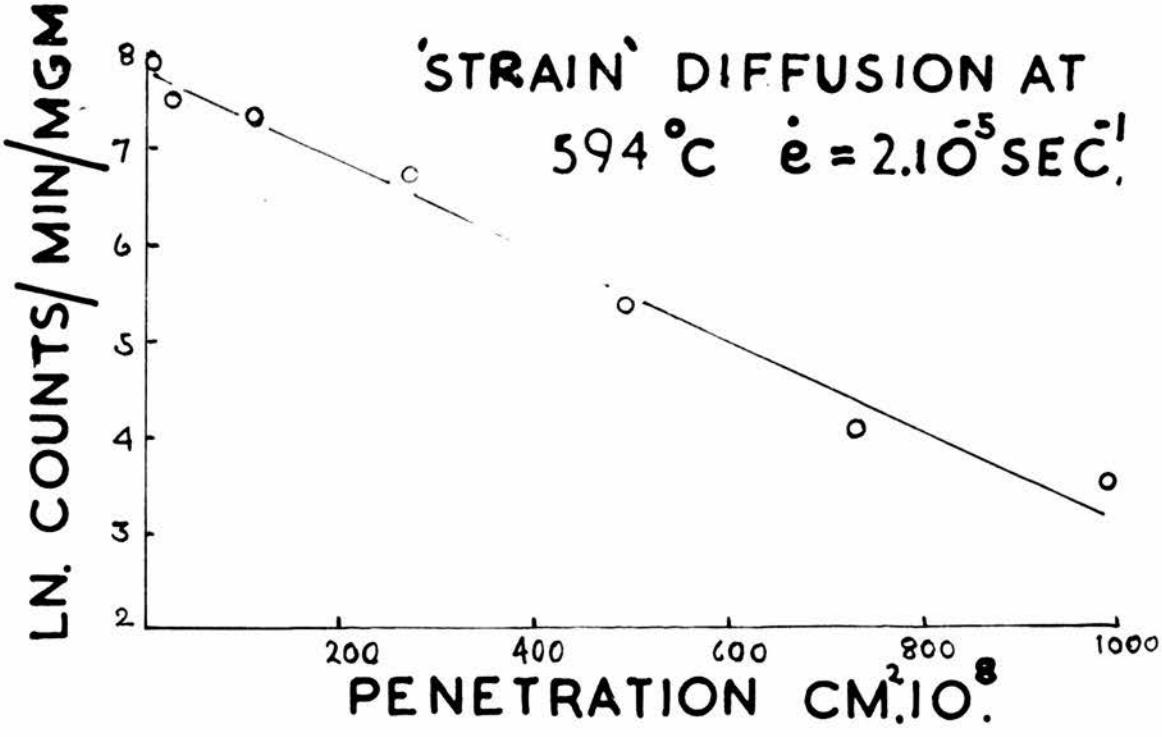
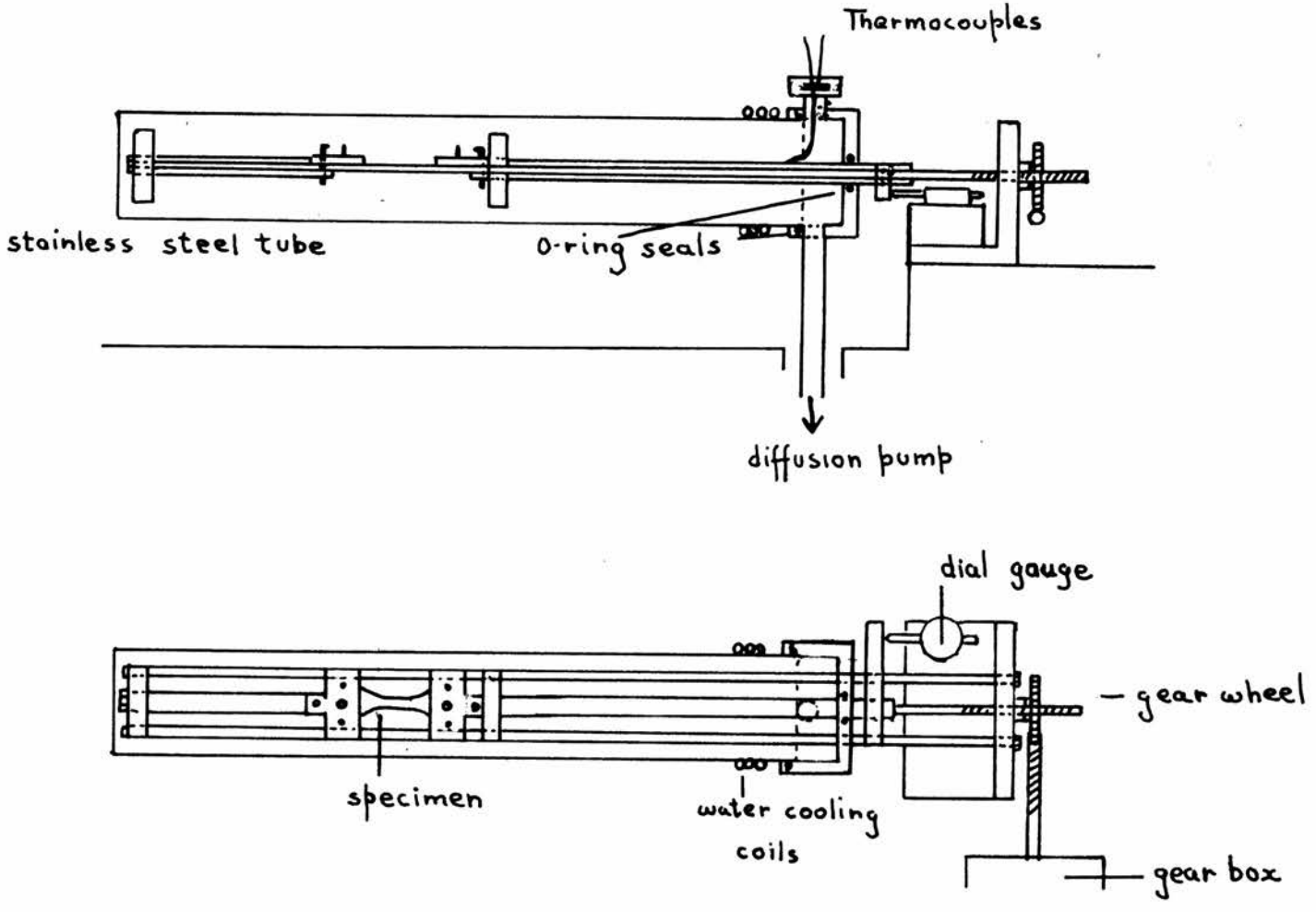


FIGURE 29.



CONSTANT STRAIN-RATE APPARATUS

FIGURE 28.

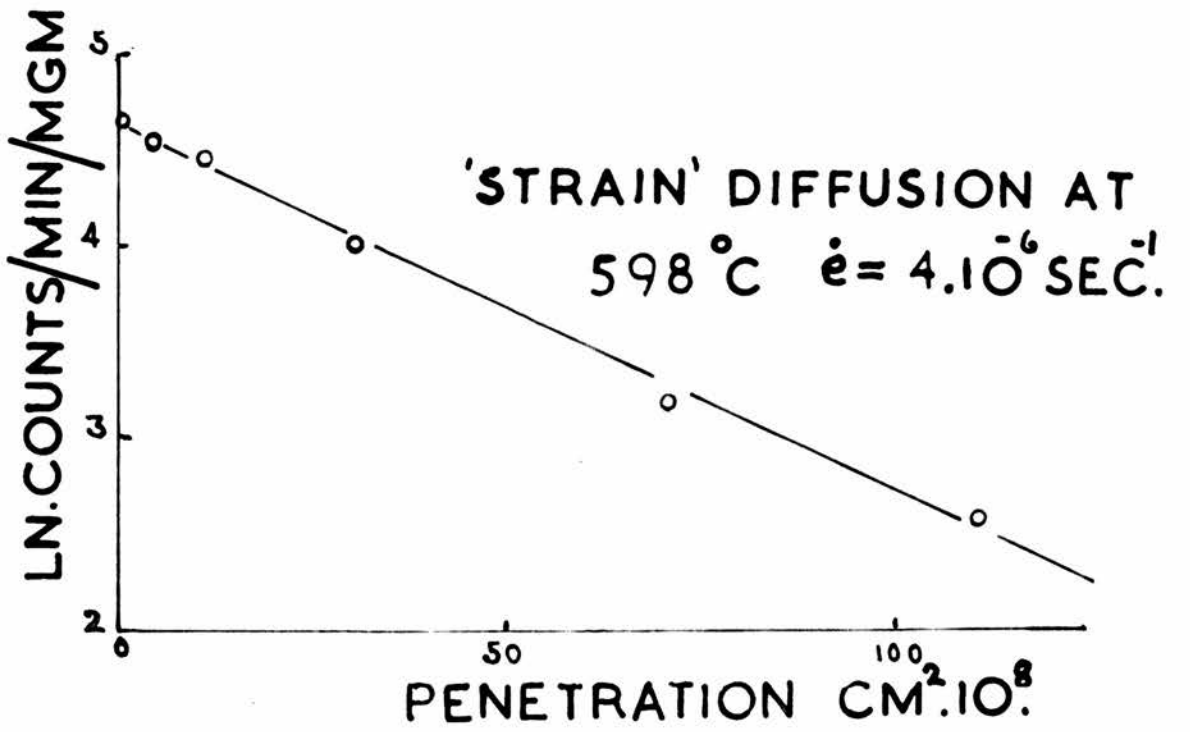


FIGURE 30.

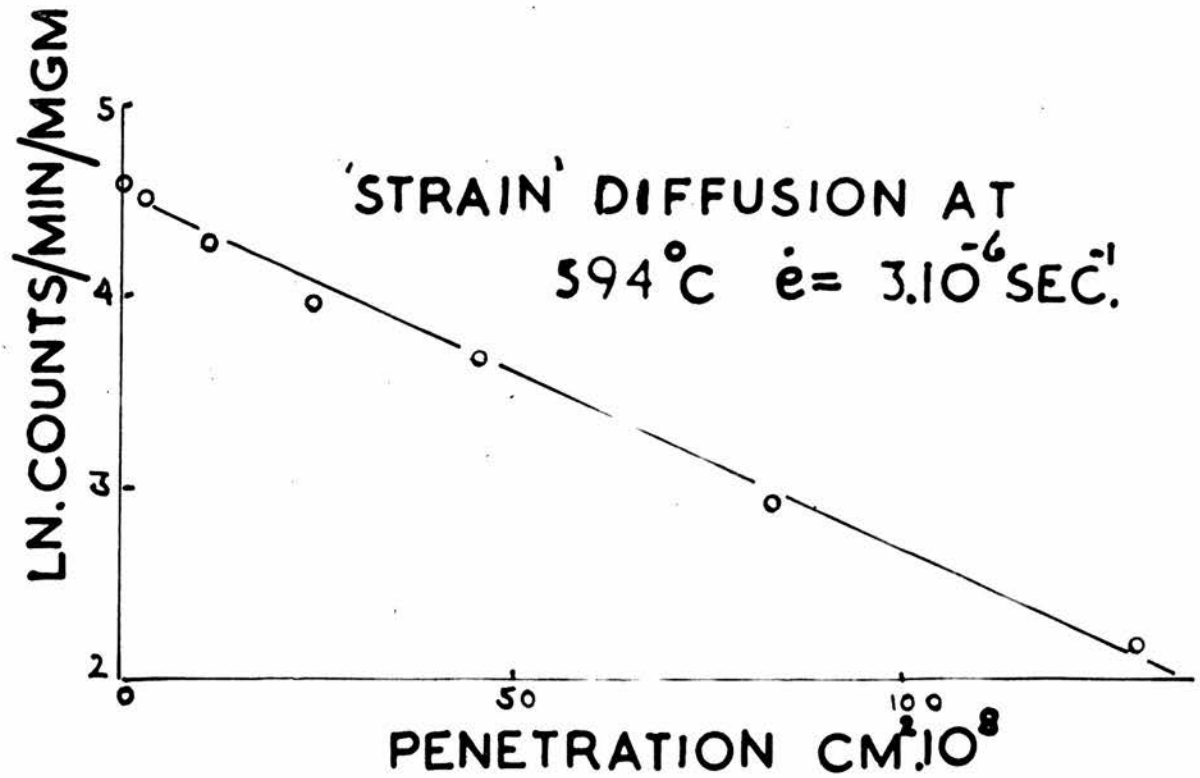
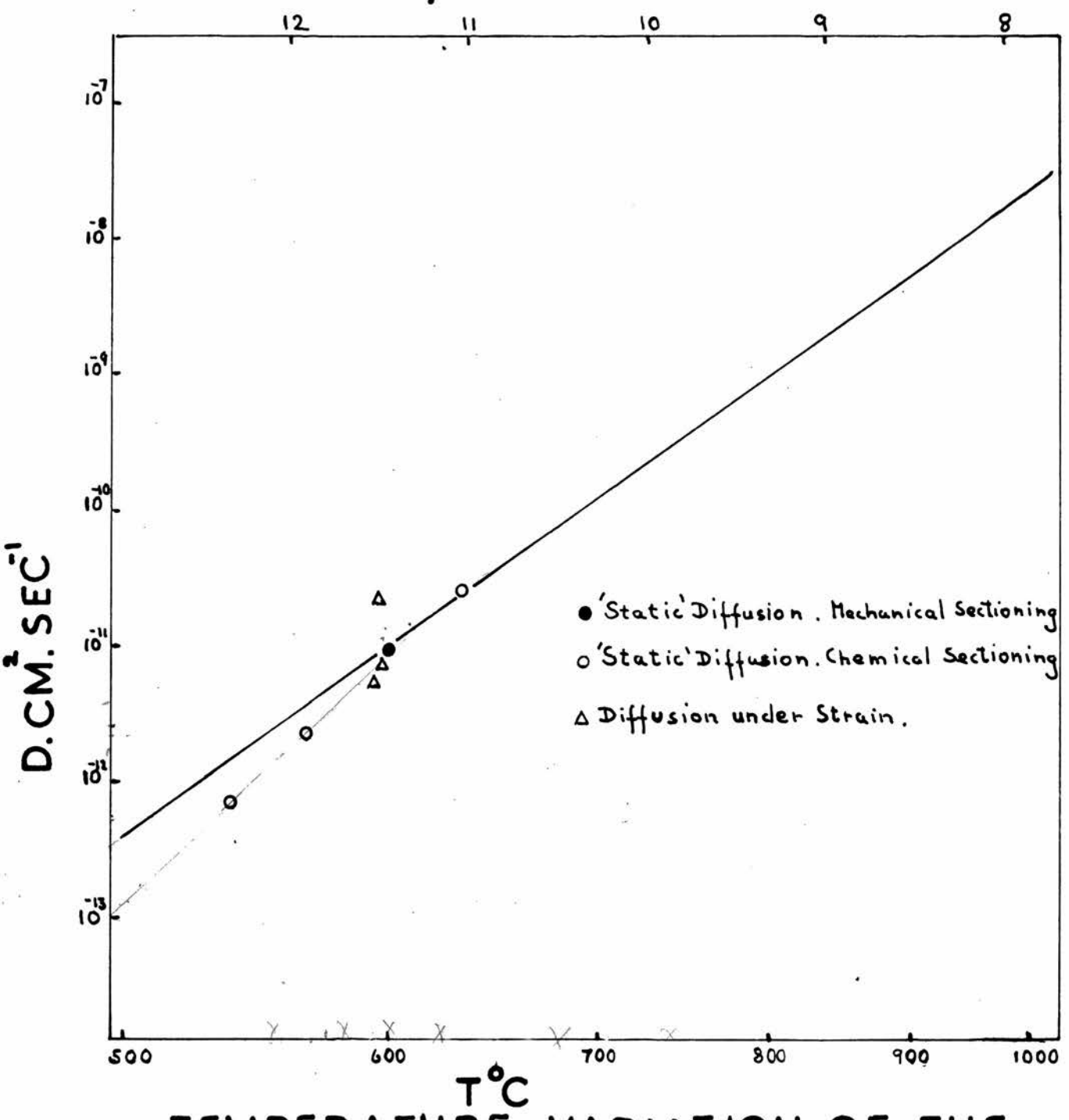


FIGURE 31.



TEMPERATURE VARIATION OF THE DIFFUSION COEFFICIENT OF ANTIMONY IN COPPER.

FIGURE 32

ACKNOWLEDGEMENTS

I wish to express my gratitude to Dr. A.F. Brown for his help and guidance during the course of this work and to thank Professor Feather for the facilities of the Natural Philosophy Department, University of Edinburgh.

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